Incorporate Elastic and Inelastic Scattering into Image Calculation for Low-Voltage Transmission Electron Microscope

Dissertation

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List of Abbreviations

AC  Aberration Corrected
CCD  Charge-Coupled Device
CTF  Contrast Transfer Function
EELS  Electron Energy-Loss Spectroscopy
FFT  Fast Fourier Transform
FWHM  Full Width at Half Maximum
HRTEM  High-Resolution Transmission Electron Microscope
MCF  Mutual Coherence Function
MDFF  Mixed Dynamic Form Factor
MOT  Mutual Object Transparency
MTF  Modulation Transfer Function
PCTF  Phase Contrast Transfer Function
POA  Phase-Object Approximation
PSF  Point Spread Function
SALVE  Sub-Angstrom Low-Voltage Electron Microscopy
SNR  Signal-to-Noise Ratio
TEAM  Transmission Electron Aberration-Corrected Microscope
TEM  Transmission Electron Microscope
WPOA  Weak Phase-Object Approximation
List of Abbreviations
List of Symbols

$C_5$ 5th-order spherical aberration
$C_M$ The Michelson contrast
$C_W$ The Weber contrast
$C_d$ The dose-dependent contrast
$C_s$ 3rd-order spherical aberration
$D$ Electron dose
$E_{fs}$ Focus spread envelope function
$E_{is}$ Image spread envelope function
$E$ Kinetic energy
$F(K)$ Elastic form factor
$S(K, K', \Delta E)$ Mixed dynamic form factor
$V$ Potential energy
$Z$ Atomic number
$\Delta f$ Defocus
$\Gamma$ Mutual coherence function
$\Omega$ Solid angle
$\Phi(r)$ Projected potential
$\Psi$ The general scattered wave
$\alpha_H$ The Bohr radius
$\alpha_s$ The Sommerfeld constant
$\beta$ Relative velocity, the ratio between $v$ and $c$
$\chi_c$ Chromatic aberration
$\chi_g$ Geometrical aberration
$\gamma$ Mutual object transparency
$\hbar$ The Planck constant
$\lambda$ The wave length of the electron wave
$\psi_0$ Incident wave
$\psi_e$ Elastic scattered wave
$\sigma$ Scattering cross section
List of Symbols

\( \theta \) Scattering angle
\( \varepsilon \) The electric constant
\( \varphi \) Azimuthal angle
\( K \) Scattering wave vector
\( \rho \) 2D plane vector
\( r \) 3D spatial vector
\( a \) The radius of one atom
\( c \) The velocity of light
\( d_i \) Instrumental resolution
\( d_s \) Specimen resolution
\( e \) The elementary charge
\( f \) Scattering amplitude
\( j \) Current density
\( k_0 \) The wave vector of the incident electron wave
\( m_e \) Non-relativistic mass of the electron
\( v \) The velocity of the electron
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Chapter 1

Overview

1.1 Motivation - Why is it necessary to calculate images?

The interpretation of HRTEM image contrast is usually not straightforward because of two reasons - firstly, the interaction between the incident electron and the sample does not behave in the way which can be described with a simple relation; secondly, the electrons passing through the sample are further deflected by the electromagnetic lens of the microscope, and the lens aberrations contribute to the difficulty of the image interpretation.

For quantitative HRTEM, these two problems are usually solved as follows: in order to minimize the interaction between the incident electrons and the samples, thin samples and high voltages are employed. On the other hand, either lens aberrations are nowadays corrected with hardware correctors or the aberration coefficients are retrieved from the recorded images and then the electron exit-wave, leaving the sample and still undistorted by the microscope lens, is numerically reconstructed.

The development of hardware corrector can be traced back to several years after the invention of the transmission electron microscope (TEM) in 1931. Scherzer stated the theorem that the spherical aberration $C_s$ and chromatic aberration $C_c$ are inevitable in a static, rotationally symmetric and space-charge-free lens [1]. He emphasized that $C_s$ and $C_c$ are the main resolution-limiting factors for the electron microscopes [2,3], and proposed the idea of an aberration corrector in 1947 [4]. Prototypes of $C_s$-correctors demonstrated the capability of $C_s$ correction [5–7]. However, the simultaneous $C_s$ correction was not yet possible [8]. The idea of compensating $C_s$ and $C_c$ at the same time with multipole correctors was later developed by Scherzer working together with Rose [9–11], and further improved by Rose’s students Haider and Zach [12–14]. Ever since the first $C_s/C_c$-corrector was realized successfully in 1980 [15], the design of $C_s/C_c$-corrector has been on the upgrade over the years. In 2009, hexapole corrector achieved the resolution of 50 pm in a 300 kV microscope, within the frame of the TEAM project [14,16,17]. The latest low-voltage $C_s/C_c$-corrector realized in SALVE (Sub-Angstrom Low-Voltage Electron Microscopy) project aims to achieve the resolution limit of 1.7 Å at 20 kV and 1.2 Å at 40 kV [18].

Based on different algorithms, the exit-wave reconstruction falls into two categories - one is based on linear imaging theory [19,26] and the other is based on nonlinear
imaging theory [27–32]. Linear (kinematic) imaging theory only considers the interaction between the incident beam and one diffracted beam, which fails for thick samples due to multiple scattering and strong interference between the diffracted beams. In the latter case methods based on nonlinear imaging theory are applied.

Are all the problems perfectly solved? Not yet. Due to the limitations of the current hardware correctors, the influence of the lens aberrations cannot be completely eliminated [33]. On the other hand, even though a remarkable step has been made towards retrieving the true structure of the sample by means of artificial neural network [32], which overcomes the limit of linear imaging theory and offers promising new insight into solving the problem of the back propagation of the dynamical scattering, it seems, increasing the accelerating voltage and using thin samples are still the most direct methods for improving the interpretation of the HRTEM images.

However, there are a number of materials which are destroyed at high accelerating voltages [34]. This problem intrigues the trend of going down to low voltages and initiated the SALVE project. The SALVE microscope is operated in the range between 20 and 80 kV [35]. Within the frame of the SALVE project, the first experimental findings on Cs-corrected HRTEM image contrast of graphene at 20 kV were reported [36]. The newcoming generation of Cs/Cc-correctors is supposed to sharpen the resolution to 172 pm at 20 kV [36], and the old dream of high-resolution imaging of radiation-sensitive organic (low Z-number) samples may soon become reality.

Under accelerating voltages as high as 300 kV, we can roughly assume that the scattering of the incident electrons by the sample atom is primarily elastic; however what if the voltage drops to as low as 20 kV? How does inelastic scattering influence the image contrast at this voltage? Furthermore, achieving the improved resolution and contrast of an aberration-corrected TEM requires an infinite electron dose on the studied specimen, and only few materials can withstand very high, let alone infinite doses. The stability of the microscope is another factor limiting the electron dose in a single image. The microscope tends to drift away from the corrected state and as a result, images can be acquired only within a small time window before resolution is deteriorated [37–39]. Also all kinds of instabilities including electrostatic and magnetic field noise [33] and instabilities caused by the sample stage can lead to blurring of the images, if the exposure time is too long.

With all this in mind, we want to study three issues in this thesis:

1. Can we use elastic model to describe the imaging process at low voltage of 20 kV?
2. How strong is inelastic scattering at 20 kV (if any) and how does it influence the image contrast?
3. How does the electron dose influence the signal-to-noise ratio (SNR), the atom contrast, as well as the resolution?

In order to study these issues, we need to utilize reasonable models under experimental conditions. A good model not only helps us to understand the imaging process in the microscope, but also aids to determine the optimal experimental conditions. Sec. 1.2 reviews the existing models applied for image calculations. In this thesis we introduce a new model for image calculation based on elastic scattering, as well as a new approximation based on an existing model for image calculation involving inelastic scattering. The global structure of the whole thesis is outlined in Sec. 1.3.
1.2 The development of models for image calculation

1.2.1 Models considering elastic scattering

Conventional models for HRTEM image calculation consider only elastic scattering and coherent interference between the electron beams. The calculation is performed by a multislice algorithm for modelling the interaction of the electron beam with the specimen, followed by a contrast transfer function (CTF) to include the geometric aberrations, and envelope functions in order to account for the finite lateral and temporal coherence of the source as well as instabilities of the microscope \cite{40, 41}. This approach is valid for weak phase object. To describe non-linear imaging, interference of the diffracted beams has to be accounted for and a non-linear transfer function (also called transmission cross-coefficient) has to be applied \cite{27, 28, 42, 43}. In addition to this first-order non-linear imaging theory, a full non-linear imaging theory was proposed by Pulvermacher \cite{44}, Rose \cite{45} and Bonevich and Marks \cite{46} \textit{(for an overview see also \cite{47})}. An interesting approach to account for damping effects by averaging the image intensity over the energy distribution of the source electrons has been reported in \cite{48–50}.

Several software packages offer programs for image calculation based on multi-slice methods, like JEMS developed by Stadelmann \cite{51}, MUSLI developed by Chuvlin \cite{52}, NCEMSS developed by O’Keefe and Kilaas \cite{53}, TEMSIM developed by Kirkland \cite{49} and QSTEM developed by Koch \cite{54}.

1.2.2 Models considering inelastic scattering

Inelastic scattering is incorporated into image calculation by means of the Mixed Dynamic Form Factor (MDFF), introduced by Rose \cite{45, 55}. The MDFF accounts for the interference of different scattered partial electron waves. The elastically scattered partial waves can interfere with each other, whereas the partial waves of the inelastically scattered electron can only interfere with each other if they correspond to the same excited object state. Schattschneider \cite{56} introduced the density matrix approach as an alternative method. The difference between the two approaches is that the MDFF describes the interference of the scattered waves in reciprocal space, and the density matrix method handles it in real space. The MDFF involves the entanglement of two waves, and the image calculation involves 4D Fourier transforms. The numerical calculation of 2D Fourier transform is usually performed by applying the fast Fourier transform (FFT). The number of arithmetic operations required for the FFT on a $N \times N$ matrix is $3N^2 \log_2 N$; however, for a $N \times N \times N \times N$ array, the number of operations increases to $6N^4 \log_2 N$, which demands $2N^2$ times of computational expenditure compared with the 2D case. The image calculation for thick objects usually involves the multislice algorithm, and the computational task required for the propagation of the 4D array through all the slices will be too time-consuming.

In order to solve the 4D problem in a computation-efficient way, different methods for the factorization of the MDFF or density matrix have been proposed with different applications \cite{56–70}. Within the core-loss range where the scattering is highly localized, Schattschneider developed the dipole approximation \cite{56} and this approximation was applied for the calculation of energy-filtered TEM images by Verbeeck et al. \cite{57}. stalknecht and Kohl \cite{58} as well as navidi-kasmai and Kohl \cite{59} proposed the calculation of the density matrix elements based on the first-order perturbation theory combined with Bloch-wave function. Dwyer et al. \cite{60, 61} calculated the density ma-
matrix elements for atomic ionization based on the work of Saldin [62]. Lugg et al. [63] computed the bound-state wave based on a relativistic Hartree-Fock model. Löffler et al. [64] introduced the method of matrix diagonalization using the spherical harmonics basis. For the low energy-loss range where the inner shell structure is neglected, Müller et al. [65, 66] utilized Bessel functions for the factorization of the MDFF obtained by employing the Raman-Compton approximation [71]. In [67–70] the MDFF was calculated by using precise wave functions. The result applies for all energy-losses, but at the sacrifice of efficiency.

1.3 The structure of this thesis

The work was carried out within the scope of the SALVE project, which aims at investigating the materials on low-voltage transmission electron microscopes operated in the range of 20-80 kV. In order to understand the mechanism of image formation for electrons accelerated under low voltages, we have developed new elastic and inelastic models based on existing method for image simulations [50, 65]. Relativistic effects are ignored in these models, because for accelerating voltages below 80 kV, the velocity of the electrons is lower than one half of the speed of light. In this case, the ratio between the relativistic and non-relativistic wavelength or electron mass is still close to 1 (Fig. 1.1).

![Figure 1.1: For the accelerating voltage of 20-80 kV, the velocity of the electron $v$ is much smaller than the light speed $c$. The ratio between the relativistic wavelength $\lambda$ and non-relativistic wavelength $\lambda_0$, as well as the ratio between the relativistic electron mass $m$ and the non-relativistic electron mass $m_e$ is still close to 1. As a result, the relativistic effect can be neglected for 20-80 kV.](image)

When being collected for imaging, the incident electrons experienced two processes in the microscope - the interaction with the sample and the modification during the propagation process within the microscope column. Chap. 2 reviews the theory of electron scattering. In Sec. 2.1 the basic concepts involving scattering cross-section, scattering amplitude and optical theorem are derived within the frame of elastic scattering, which was written based on Glauber’s and Rose’s lecture notes [72, 73]. This section also dis-
1.3. THE STRUCTURE OF THIS THESIS

cusses the concepts of the weak phase-object approximation (WPOA), the phase-object approximation (POA) and the application of POA in the multislice method. In the first part of Sec. 2.2, the concepts based on elastic scattering are extended for inelastic scattering. The remaining part of the Sec. 2.2 highlights the concepts employed by the mutual coherence approach [45, 55], which handles inelastic scattering in image calculations. These concepts include the mutual coherence function (MCF), the mixed dynamic form factor (MDFF) and the mutual object transparency (MOT).

Chap. 3 describes the elements which modify the scattered electrons during the propagation process in the microscope column, including the geometrical and chromatic aberrations of the electromagnetic lenses, electromagnetic and mechanical instabilities and the MTF of the camera.

Part II introduces the experiment settings (Chap. 4) as well as the details of the samples (Chap. 5) used for calculations.

Part III presents the results in three chapters. Each chapter is adapted from one publication. Chap. 6 (based on [74]) introduces the model for image calculation involving elastic scattering by incorporating the experimental zero-loss peak extracted from the EELS spectra. The image calculation verifies the validity of WPOA for graphene imaged at 80 kV. We show that the WPOA based on pure elastic scattering fails for 20 kV. This leads to the discussion of the influence of inelastic scattering at 20 kV in Chap. 7, which is based on [75].

The method of image calculation considering inelastic scattering (Chap. 7) is based on the multislice mutual coherence method outlined in [65, 66] and concentrates on the low electron-energy-loss range. In addition, a new approximation for the MDFF is introduced. This approximation keeps the maximum similarity with the MDFF function, obtained by utilizing the Raman-Compton model [71] and the Wentzel model [76] for the atom potential. One key results is that our approximation can be applied to different imaging conditions, without loss of computational efficiency.

Experimental images are recorded with finite electron dose. In order to quantitatively compare the calculated and experimental images, it is necessary to take the electron dose into account. Chap. 8 (based on [77]) serves this purpose and explores the dependence of the signal-to-noise ratio (SNR), the atom contrast and the specimen resolution on the electron dose and the sampling of the camera, by means of a method considering finite electron dose, which is extended from the elastic model introduced in Chap. 6. A modified definition of the atom contrast considering finite electron dose is introduced, and this definition is more reasonable for evaluating the object visibility in the experimental images than other existing contrast definitions.

Finally, Part IV ends the whole work with a summary.
Part I

Theory
Chapter 2

Theory of electron scattering

With the relativistic effect ignored, the propagation of an electron wave \( \Psi(r, t) \) is described by the Schrödinger equation:

\[
\frac{-\hbar^2}{2m_e} \Delta \Psi(r, t) + V(r, t)\Psi(r, t) = i\hbar \frac{\partial \Psi(r, t)}{\partial t}.
\] (2.1)

Here \( m_e \) is the non-relativistic mass of the electron, \( \hbar \) is the Planck constant and \( V(r, t) \) is its potential energy.

The electron wave keeps its original propagating direction in field-free space. An electromagnetic field deflects the electron from its original path and the process is defined as scattering. The scattering is elastic if it involves only momentum transfer without energy loss. In this case, the potential is static, \( V(r, t) = V(r) \) and the wave function has the form

\[
\Psi(r, t) = \Psi(r) e^{-iEt/\hbar}.
\] (2.2)

By substituting Eq. (2.2) for \( \Psi(r, t) \) in Eq. (2.1), we obtain the time-independent Schrödinger equation

\[
\frac{-\hbar^2}{2m_e} \Delta \Psi(r) + V(r)\Psi(r) = E\Psi(r).
\] (2.3)

For elastic scattering, we can neglect the time evolution of the wave and the incident wave \( \psi_0 \) is a solution of the Schrödinger equation (Eq. (2.3)). After elastic scattering, the outgoing wave

\[
\Psi_0 = \psi_0 + \psi_e,
\] (2.4)

which consists of the incident wave \( \psi_0 \) and the elastically scattered wave \( \psi_e \), is also a solution of Eq. (2.3).

Inelastic scattering is accompanied by both momentum and energy transfer, and the potential is time-dependent. By including the incident electron and the scattering object as a whole system, we can rewrite the Schrödinger equation as

\[
i\hbar \frac{\partial}{\partial t} \Psi(r, r', t) = \hat{H}\Psi(r, r', t).
\] (2.5)
In a simplified case where the scattering object contains only one atom with the atomic number $Z$, the Hamiltonian operator $\hat{H}$ for the whole system includes the following terms:

$$\hat{H} = -\frac{\hbar^2}{2m_e} \Delta_r + Z \sum_{\nu = 1}^{Z} \left[ -\frac{\hbar^2}{2m_e} \Delta_r + \sum_{\mu < \nu} \frac{e^2}{4\pi \varepsilon_0 |r_\nu - r_\mu|} \right] - \frac{Ze^2}{4\pi \varepsilon_0 |r_\nu - R|} \sum_{\mu < \nu} \frac{e^2}{4\pi \varepsilon_0 |r - r_\nu|}.$$

Here $r$, $r_\nu$, and $R$ are the positional vectors of the incident electron, the $\nu$th object electron and the atomic nucleus, respectively. The first two terms in Eq. (2.6) correspond to the kinetic energy of the incident electron and the object electrons, respectively. The last four terms in Eq. (2.6) describe the Coulomb interactions between different charged particles.

During inelastic scattering, the object is excited to any of its eigenstates $|j\rangle$. Neglecting the exchanging effect between the incident electron and the object electron, we can write the wave function corresponding to each object eigenstate as the product of the scattered electron wave and the object state. The wave function of the whole system $\psi_t$ is the sum of all the coupled states:

$$\psi_t(r, r_o, t) = \sum_{j=0}^{\infty} \Psi_j(r, t) \phi_j(r_o) e^{-iE_j t/\hbar} \Leftrightarrow \psi_t = \sum_{j=0}^{\infty} |j\rangle \psi_j.$$  

Here $E_j$ is the energy of the object at the eigenstate $|j\rangle$. The case $j = 0$ corresponds to the elastic scattering and the object state $\phi_j(r_o)$ is an ensemble state of all the electrons in the object:

$$\phi_j(r_o) = \phi_j(r_1, r_2, \cdots r_Z).$$

The eigenstates of the object are mutually orthogonal and form a complete set:

$$\int \cdots \int \phi_m^*(r') \phi_j(r') dr'_1 \cdots dr'_Z = \delta_{mj} \Leftrightarrow \langle m|j\rangle = \delta_{mj}.$$  

$$\sum_{j=0}^{\infty} \phi_j(r) \phi_j^*(r') = \delta(r_1 - r'_1) \cdots \delta(r_Z - r'_Z) \Leftrightarrow \sum_{j=0}^{\infty} |j\rangle \langle j| = I.$$  

In the following some basic concepts used for elastic scattering are reviewed in Sec. 2.1 which include the scattering cross-section (Sec. 2.1.1), the optical theorem (Sec. 2.1.2) and the scattering amplitude (Sec. 2.1.3). The important methods applied for image calculations including the phase object approximation (Sec. 2.1.4) and multislice algorithm (Sec. 2.1.5) are also discussed. Sec. 2.2 continues the discussion on inelastic scattering. Sec. 2.2.1 extends the concepts applied for elastic scattering to inelastic scattering. Sec. 2.2.2-2.2.4 put emphasis on the concepts of the MDFF and the MOT, which are utilized for the image calculation involving inelastic scattering. Sec. 2.2.5 outlines the general procedure for image calculation involving inelastic scattering.
2.1 Elastic scattering

For plane-wave illumination, the incident wave is written as:

\[ \psi_0 = e^{ik_0 r}. \]  

(2.11)

Here \( k_0 \) is the wave vector carrying the information on the energy and propagation direction of the incident wave. The momentum transfer during elastic scattering is a function of the scattering angle \((\theta, \varphi)\) and the angle-dependent scattering probability is determined by the scattering amplitude \( f(\theta, \varphi) \). The scattered wave has the form:

\[ \psi_e = f(\theta, \varphi) e^{ik_0 r} \frac{1}{r}. \]  

(2.12)

Here \( r \) in the denominator of Eq. (2.12) indicates that the amplitude of the spherical wave decreases as it propagates away from the scattering center. The term \( f(\theta, \varphi) \) implies that the scattering amplitude is not homogeneous in all directions, but stronger in certain directions and weaker in others. For a point scatterer, the total wave after elastic scattering becomes:

\[ \Psi_0 = \psi_0 + \psi_e = e^{ik_0 r} + f(\theta, \varphi) e^{ik_0 r} \frac{1}{r}. \]  

(2.13)

Figure 2.1: Scattering geometry. The incident plane wave with the wave vector \( k_0 \) propagates through the area \( d\sigma \), and exit the area \( dS \) after being scattered. the wave has the spherical form. The strength of the scattered wave amplitude depends on the scattering angle \((\theta, \varphi)\). The solid angle is defined as \( d\Omega = dS/r^2 = \sin \theta d\theta d\varphi \).

2.1.1 Scattering cross-section

The electric current during the scattering is a constant, which leads to the following relation based on the scattering geometry (Fig. 2.1):

\[ \int j_0 \cdot n_\sigma d\sigma = \int j_e \cdot n_S r^2 d\Omega, \]  

(2.14)

where \( j_0 \) and \( j_e \) are the incoming and outgoing current density as vectors, respectively. The terms \( n_\sigma \) and \( n_S \) are the unit normal vectors of the planes \( d\sigma \) and \( dS \), respectively.
The current density $j_0$ and $j_e$ are defined in non-relativistic quantum mechanics as

$$j_0 = \frac{\hbar}{2m_e i} (\psi_0 \nabla \psi_0^* - \psi_0^* \nabla \psi_0), \quad (2.15)$$

$$j_e = \frac{\hbar}{2m_e i} (\psi_e \nabla \psi_e^* - \psi_e^* \nabla \psi_e). \quad (2.16)$$

Based on Eqs. (2.11) and (2.12), we obtain the following relations:

$$\nabla \psi_0 = i k_0 e^{ik_0 r}, \quad (2.17)$$

$$\nabla \psi_0^* = -i k_0 e^{-ik_0 r}, \quad (2.18)$$

$$\nabla \psi_e = f(\theta, \phi) \left( i k_0 r e^{ik_0 r} r \theta - r e^{ik_0 r} r \phi \right), \quad (2.19)$$

$$\nabla \psi_e^* = f^*(\theta, \phi) \left( -ik_0 r e^{-ik_0 r} r \theta - r e^{-ik_0 r} r \phi \right). \quad (2.20)$$

Combining Eqs. (2.14)-(2.20) results in

$$\int k_0 \cdot n_\sigma d\sigma = \hat{\int} \left| f(\theta, \phi) \right|^2 \frac{k_0}{r} r \cdot n_S d\Omega. \quad (2.21)$$

For axial plane-wave illumination, $k_0$ is perpendicular to the planes $d\sigma$ (Fig. 2.1). Therefore we obtain

$$k_0 \cdot n_\sigma = |k_0||n_\sigma| \cos(k_0, n_\sigma) = k_0. \quad (2.22)$$

For the scattered spherical wave, the radius vector $r$ always lies in the normal direction of the plane $dS$, we have

$$r \cdot n_S = |r||n_S| \cos(r, n_S) = r. \quad (2.23)$$

Therefore Eq. (2.21) can be written as

$$\sigma = \int d\sigma = \int |f(\theta, \phi)|^2 d\Omega = \int_0^{2\pi} \int_0^\pi |f(\theta, \phi)|^2 \sin \theta d\theta d\phi. \quad (2.24)$$

Here $\sigma$ is the total elastic scattering cross section, which can also be written as

$$\sigma = \int \frac{d\sigma}{d\Omega} d\Omega. \quad (2.25)$$

By comparing Eqs. (2.24) and (2.25), we can define the differential scattering cross section for elastic scattering as

$$\frac{d\sigma}{d\Omega} = |f(\theta, \phi)|^2. \quad (2.26)$$

### 2.1.2 Optical theorem

The optical theorem describes the relation between the forward scattering amplitude and the total scattering cross section. The essence of optical theorem is particle (or probability) conservation, indicating that the amount of incoming and outgoing particles should stay the same. In the case of elastic scattering, the wave function $\Psi(r, t)$ has the form in Eq. (2.2) and time derivative of the probability density $n(r, t) = \Psi(r, t)\Psi^*(r, t)$
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results in 0:

\[ \frac{\partial n}{\partial t} = \frac{\partial (\Psi \Psi^*)}{\partial t} = \Psi \frac{\partial \Psi^*}{\partial t} + \Psi^* \frac{\partial \Psi}{\partial t} = 0. \]  \hspace{1cm} (2.27)

Based on time-dependent Schrödinger equation (Eq. (2.1)), we obtain

\[ \frac{\partial (\Psi \Psi^*)}{\partial t} = \frac{\hbar}{2m_e} \left[ \Psi \nabla^2 \Psi^* - \Psi^* \nabla^2 \Psi \right] = \frac{\hbar}{2m_e} \nabla \cdot [\Psi \nabla \Psi^* - \Psi^* \nabla \Psi] = \frac{\hbar}{m_e} \nabla \cdot \text{Im} [\Psi \nabla \Psi^*]. \]  \hspace{1cm} (2.28)

Combining Eqs. (2.27) and (2.28), we end up with

\[ \nabla \cdot \text{Im} [\Psi \nabla \Psi^*] = 0. \]  \hspace{1cm} (2.29)

According to Gauss’s theorem, volume integral of the gradient can be transformed into surface integral. Integrating Eq. (2.29) over the volume of sphere with the radius \( r \), we obtain the relation

\[ \iiint \nabla \cdot \text{Im} [\Psi \nabla \Psi^*] \, d^3r = \iint \text{Im} [\Psi \nabla \Psi^*] \cdot \mathbf{n}_S \, dS = 0. \]  \hspace{1cm} (2.30)

Here \( dS \) is a small area on the surface of the large sphere and \( \mathbf{n}_S \) is the unit normal vector of the area \( dS \). Substituting the total wave (Eq. (2.13)) for \( \Psi \) into Eq. (2.30), we obtain

\[ \iint (\Psi_0 \nabla \rho_0^* - \rho_0^* \nabla \rho_0) \cdot \mathbf{n}_S \, dS = \iint (\psi_0 \nabla \rho_0^* - \rho_0^* \nabla \psi_0) \cdot \mathbf{n}_S \, dS \\
+ \iint (\psi_e \nabla \rho_e^* - \rho_e^* \nabla \psi_e) \cdot \mathbf{n}_S \, dS \\
+ \iint (\rho_0 \nabla \psi_e^* - \psi_e^* \nabla \rho_0) \cdot \mathbf{n}_S \, dS \\
+ \iint (\rho_e \nabla \psi_0^* - \psi_0^* \nabla \rho_e) \cdot \mathbf{n}_S \, dS = 0. \]  \hspace{1cm} (2.31)

Since the incident wave \( \psi_0 = e^{i k_0 r} e^{-i E t / \hbar} \) is a solution of Schrödinger equation (Eq. (2.1)) and satisfies \( \partial (\psi_0 \rho_0^*) / \partial t = 0 \), one can already conclude that the first integral results in 0. This result can also be verified with the help of Eqs. (2.17) and (2.18). We can ignore the factor \( e^{-i E t / \hbar} \) in the surface integral in Eq. (2.31), and obtain

\[ \psi_0 \nabla \rho_0^* - \rho_0^* \nabla \psi_0 = -2 i k_0 \]

\[ \iint (\psi_0 \nabla \rho_0^* - \rho_0^* \nabla \psi_0) \cdot \mathbf{n}_S \, dS = -2 i \iint k_0 \cdot \mathbf{n}_S \, dS. \]  \hspace{1cm} (2.32)

Substituting the relation \( k_0 \cdot \mathbf{n}_S = k_0 \cos \theta \) and \( dS = r^2 \sin \theta \, d\theta \, d\phi \) into the first integral in Eq. (2.31), we get

\[ -2 i \iint k_0 \cdot \mathbf{n}_S \, dS = -2 i r^2 \int_0^{2\pi} d\phi \int_0^\pi k_0 \cos \theta \sin \theta \, d\theta = 0. \]  \hspace{1cm} (2.33)
Similarly, with the help of Eqs. (2.19) and (2.20) we obtain
\[
\psi_e \nabla \psi_e^* - \psi_e^* \nabla \psi_e = -2i|f(\theta, \varphi)|^2 \frac{k_0}{r^3} r.
\] (2.34)

Therefore the second integral in Eq. (2.31) becomes
\[
\iint (\psi_e \nabla \psi_e^* - \psi_e^* \nabla \psi_e) \cdot nS dS = -2ik_0 \int |f(\theta, \varphi)|^2 \frac{r}{r} \cdot nS d\Omega. \tag{2.35}
\]

Because the radius vector \( r \) lies in the direction parallel to the normal vector \( n_S \) of the plane \( dS \), we get \( r \cdot n_S = r \) and
\[
\iint (\psi_e \nabla \psi_e^* - \psi_e^* \nabla \psi_e) \cdot nS dS = -2ik_0 \int |f(\theta, \varphi)|^2 d\Omega = -2ik_0 \sigma. \tag{2.36}
\]

For the third integral in Eq. (2.31), we obtain first with the help of Eqs. (2.17) and (2.20):
\[
\psi_0 \nabla \psi_e^* - \psi_e^* \nabla \psi_0 = f^*(\theta, \varphi) e^{i(k_0r - kr)} (-\frac{i k_0}{r} - \frac{i k_0 r}{r^2} - \frac{r}{r^3}). \tag{2.37}
\]

By introducing \( dS = r^2 \sin \theta d\theta d\varphi \) based on the same spherical geometry as in Fig. 2.1, we obtain further
\[
\iint (\psi_0 \nabla \psi_e^* - \psi_e^* \nabla \psi_0) \cdot nS dS \nonumber \]
\[
= \int_0^{2\pi} \int_0^\pi f^*(\theta, \varphi) e^{ik_0r(\cos \theta - 1)} [-ik_0r(\cos \theta + 1) - 1] \sin \theta d\theta d\varphi 
\]
\[
= -\int_0^{2\pi} \int_0^\pi f^*(\theta, \varphi) e^{ik_0r(\cos \theta - 1)} ik_0 r(\cos \theta + 1) \sin \theta d\theta d\varphi 
\]
\[
-\int_0^{2\pi} \int_0^\pi f^*(\theta, \varphi) e^{ik_0r(\cos \theta - 1)} \sin \theta d\theta d\varphi. \tag{2.38}
\]

The first integral with respect to \( \theta \) in Eq. (2.38) can be evaluated with partial integration as follows:
\[
= \int_0^\pi f^*(\theta, \varphi) e^{ik_0r(\cos \theta - 1)} ik_0 r(\cos \theta + 1) \sin \theta d\theta 
\]
\[
= f^*(\theta, \varphi) e^{ik_0r(\cos \theta - 1)}(\cos \theta + 1) \bigg|_0^\pi - \int_0^\pi \left[ f^*(\theta, \varphi)(\cos \theta + 1) \right]^' e^{ik_0r(\cos \theta - 1)} d\theta \tag{2.39}
\]
\[
= -2f^*(0) - \int_0^\pi \frac{df^*(\theta, \varphi)}{d\theta} (\cos \theta + 1) e^{ik_0r(\cos \theta - 1)} d\theta + \int_0^\pi f^*(\theta, \varphi) \sin \theta e^{ik_0r(\cos \theta - 1)} d\theta.
\]

For the case \( \theta = 0 \), \( f(\theta, \varphi) \) is independent of \( \varphi \) (Fig. 2.1), therefore we can replace \( f^*(0, \varphi) \) with \( f^*(0) \). For the second integral in Eq. (2.39), when \( \theta \) is not close to 0, the exponent \( e^{ik_0r(\cos \theta - 1)} \) oscillates fast around 0 because \( k_0 r \gg 1 \). Hence in this case, the integral containing the product of \( e^{ik_0r(\cos \theta - 1)} \) and a finite function \( (\cos \theta + 1)df^*(\theta, \varphi)/d\theta \) is trivial. On the other hand, the scattering is approximately forward when \( \theta \to 0 \), and thus the change of \( f^*(\theta, \varphi) \) with respect to \( \theta \) is negligible, resulting in \( df^*(\theta, \varphi)/d\theta \to 0 \). Consequently, the second term in Eq. (2.39) vanishes. The last term in Eq. (2.39) cancels with the second integral in Eq. (2.38) with respect to \( \theta \). Finally,
we obtain
\[ \oint (\psi_0 \nabla \psi_e^* - \psi_e^* \nabla \psi_0) \cdot \mathbf{n} S dS = -2f^*(0) \int_0^{2\pi} d\phi = -4\pi f^*(0). \]  
(2.40)

The fourth integral in Eq. (2.31) is the opposite conjugate of the third integral, which results in
\[ \oint (\psi_e^* \nabla \psi_0 - \psi_0 \nabla \psi_e^*) \cdot \mathbf{n} S dS = 4\pi f(0). \]  
(2.41)

Substituting Eqs. (2.33), (2.36), (2.40) and (2.41) into Eq. (2.31), we obtain
\[ \frac{4\pi}{k_0} \text{Im} f(0) = \sigma. \]  
(2.42)

Based on the optical theorem (Eq. (2.42)), we can draw some useful conclusions. Firstly, the scattering amplitude is a complex. Secondly, in order to measure the total scattering cross section, it is not necessary to locate many detectors in all scattering directions for collecting all the outgoing electrons. Instead, only one detector in the forward direction is sufficient, and the distance between the detector and the sample should be large enough so that only the forward scattered electrons are collected.

### 2.1.3 Scattering amplitude

Non-relativistic time-independent Schrödinger equation (Eq. (2.3)) can be solved with the help of Green’s function (Appendix A), and the solution is the Liouville-Neumann-Born series:
\[ \Psi(r) = e^{ik_0 r} - \frac{m_e}{2\pi \hbar^2} \int \int \frac{e^{ik_0 |r-r'|}}{|r-r'|} V(r') \Psi(r') d^3 r', \]  
(2.43)

The solution is a series because it is solved by iterations. The first Born approximation is obtained by replacing \( \Psi(r') \) in Eq. (2.43) with the incident wave \( e^{ik_0 r'} \):
\[ \Psi_1(r) = e^{ik_0 r} - \frac{m_e}{2\pi \hbar^2} \int \int \frac{e^{ik_0 |r-r'|}}{|r-r'|} V(r') e^{ik_0 r'} d^3 r'. \]  
(2.44)

The second-order Born approximation is obtained by substituting \( \Psi_1(r') \) for \( \Psi(r') \) in Eq. (2.43), etc.

In a transmission electron microscope the diffraction pattern is recorded in the back-focal plane of the objective lens. In this case the distance \( r \) between a point on the sample and the detector is usually much larger than the distance \( r' \) between two points on the sample (Fig. 2.2). Therefore, we can use the approximations in the Fraunhofer region:
\[ |r-r'| = \sqrt{|r-r'|^2} \approx \sqrt{1 - \frac{2r'r}{r^2}} \approx |r - \frac{r'r}{r}|, \]  
(2.45)
\[ \frac{1}{|r-r'|} \approx \frac{1}{r} \frac{1}{(1 - \frac{r'r}{r^2})} \approx \frac{1}{r} \frac{1}{(1 + \frac{rr'}{r^2})} \approx \frac{1}{r}. \]  
(2.46)
Writing \( \mathbf{k}_r = k_0 \frac{\mathbf{r}}{r} \), one can express Eq. 2.43 as
\[
\Psi(r) = e^{i k_0 r} - \frac{m_e e^{i k_0 r}}{2 \pi \hbar^2} \int \int \int e^{-i k_r r'} V(r') \Psi(r') d^3 r'.
\]
We define the elastic scattering amplitude
\[
f(k_r, k) = -\frac{m_e}{2 \pi \hbar^2} \int \int \int e^{-i k_r r'} V(r') \Psi_k(r') d^3 r',
\]
where \( \Psi_k(r') \) indicates that the wave vector of the wave \( \Psi \) is \( \mathbf{k} \). Eq. (2.47) can therefore be transformed into the form of Eq. (2.13):
\[
\Psi(r) = e^{i k_0 r} + \frac{e^{i k_0 r}}{r} f(k_r, k).
\]
Replacing \( \Psi_k(r') \) with the incident wave vector \( e^{i k_0 r'} \) in Eq. (2.48), we obtain the scattering amplitude \( f(k_r, k_0) \) for the first-order Born approximation:
\[
f(k_r, k_0) = -\frac{m_e}{2 \pi \hbar^2} \int \int \int e^{-i (k_r - k_0) r'} V(r') d^3 r'.
\]
Eq. (2.50) indicates that the scattering amplitude for the first-order Born approximation is proportional to the Fourier transform of the potential energy. It is worth mentioning here that the elastic scattering amplitude is not equal to the elastic form factor, which is the Fourier transform of the electron density.

Within the frame of the first-order Born approximation, the incident wave has only been scattered once. This is true for very thin samples in the microscope. However, as the sample thickness increases, multiple scattering cannot be neglected and the first-order Born approximation is not valid anymore.

For forward scattering along the optical axis with \( k_r = k_0 \), we have
\[
f(k_r, k_0) = f(0) = -\frac{m_e}{2 \pi \hbar^2} \int \int \int V(r') d^3 r'.
\]
According to the optical theorem (Sec. 2.1.2), the total scattering cross section is proportional to the imaginary part of the forward scattering amplitude. However, Eq. (2.51) indicates that \( f(0) \) is a real number because the potential energy \( V(r') \) is real, which shows that the first Born approximation violates the optical theorem and hence does not conserve the number of scattered particles.

### 2.1.4 Phase-object approximation (POA)

Within the frame of POA, we assume that when the incident electron wave passes through a thin sample, the atoms in the sample work like thin lenses and only modify the phase shift of the incident wave. We also assume that there is no back scattering during the process. This approximation is valid under the following conditions:

1. The wavelength of the electron \( \lambda \) is much smaller compared with the radius of the atom \( a \) in the sample: \( \lambda/a \ll 1 \);
2. The sample thickness \( \Delta z \) is small enough: \( \Delta z < a^2/\lambda \);
3. The kinetic energy of the electron is much larger than its potential energy.
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Figure 2.2: The vector relation for the scattering by a thin object. \( \theta = 0 \) indicates forward scattering and \( \theta = \pi \) indicates back scattering.

The wave propagating through the sample is expressed as

\[
\Psi(r) = e^{ik_0r} T(r). \tag{2.52}
\]

Here \( T(r) \) is defined as the transmission function and it introduces the extra phase shift to the incident wave \( e^{ik_0r} \). Dividing Eq. (2.43) by the incident wave \( e^{ik_0r} \), we obtain the function \( T(r) \):

\[
T(r) = 1 - \frac{m_e}{2\pi \hbar^2} \int \frac{e^{ik_0|r-r'|} - i k_0 (r-r')}{|r-r'|} V(r') T(r') d^3r'. \tag{2.53}
\]

We introduce \( r'' = r - r' \) and Eq. (2.53) becomes

\[
T(r) = 1 + \frac{m_e}{2\pi \hbar^2} \int \frac{e^{ik_0r''} - i k_0 r'''}{r'''} V(r - r'') T(r - r''') d^3r'''

\[
= 1 + \frac{m_e}{2\pi \hbar^2} \int_0^\infty \int_0^{2\pi} \int_0^\pi r'' e^{ik_0r''(1-\cos \theta)} V(r - r'') T(r - r''') \sin \theta d\theta d\phi dr'''. \tag{2.54}
\]

The integral with respect to \( \theta \) in Eq. (2.54) is evaluated with partial integration as follows:

\[
\int_0^\pi e^{ik_0r''(1-\cos \theta)} V(r - r'') T(r - r''') \sin \theta d\theta
\]

\[
= \frac{1}{ik_0r''} e^{ik_0r''(1-\cos \theta)} V(r - r'') T(r - r''') \bigg|_0^\pi \tag{2.55}
\]

\[
- \frac{1}{ik_0r''} \int_0^\pi [V(r - r'') T(r - r''')]' e^{ik_0r''(1-\cos \theta)} d\theta.
\]

When \( \theta \) is not close to 0, the exponent \( e^{ik_0r''(1-\cos \theta)} \) oscillates fast around 0 because \( k_0r'' \gg 1 \), therefore the integral in Eq. (2.55) is trivial in this case. For \( \theta \to 0 \), the term \( V(r - r'') T(r - r''') = V(r') T(r') \) changes slowly with respect to \( \theta \), because in
this case \( r' \) lies approximately parallel to \( k_0 \) and a slight change of \( \theta \) barely changes the direction or the magnitude of \( r' \). Hence the integral in Eq. (2.55) can be neglected. In the first part, the case \( \theta = \pi \) corresponds to the situation where \( r'' \) lies anti-parallel to \( k_0 \) (Fig. 2.2). The physical meaning in this case is that the incident wave arrives at the surface of the sample and gets totally reflected without propagation through the sample. This contradicts our assumption that there is no back scattering in the process. Since \( \theta = \pi \) indicates that there is no outgoing wave, \( T(r') \) is therefore 0 for this case.

The remaining case \( \theta = 0 \) indicates that \( r'' \) lies parallel to \( k_0 \), representing forward scattering. The transmission function \( T(r') \) in Eq. (2.54) reduces to

\[
T(r') = 1 + \frac{i m_e}{2\pi \hbar^2 k_0} \int_0^{2\pi} \int_0^\infty V(r - r'')T(r - r'') d\varphi dr''
\]

\[
= 1 + \frac{i}{2\pi \hbar v} \int_0^{2\pi} \int_0^\infty V(r - r'')T(r - r'') d\varphi dr''.
\]

(2.56)

For forward scattering the vectors \( r' \) and \( r'' \) lie parallel to the incident wave vector \( k_0 \) (Fig. 2.2), and \( V(r')T(r') \) is independent of the azimuth angle \( \varphi \) which lies within the plane normal to \( k_0 \). Therefore, the integral with respect to \( \varphi \) in Eq. (2.56) results in \( 2\pi \). The integral in three dimensions (Eq. (2.54)) finally reduces to an integral in one dimension along the direction of forward scattering, which is perpendicular to the sample plane (Fig. 2.2). We substitute \( r' = r - r'' \) back to Eq. (2.56) and decompose the vector \( r' \) in two components - the in-plane vector \( \rho \) and the scalar \( z \) lying perpendicular to the plane. The integral with respect to \( r'' \) in Eq. (2.56) becomes an integral with respect to \( z \):

\[
T(\rho, z) = 1 + \frac{i}{\hbar v} \int_{-\infty}^{\infty} V(\rho, z')T(\rho, z') dz'
\]

\[
= 1 - \frac{i}{\hbar v} \int_{-\infty}^{\infty} V(\rho, z')T(\rho, z') dz'.
\]

(2.57)

The solution of Eq. (2.57) is

\[
T(\rho, z) = e^{-i \frac{\hbar v}{\rho} \int_{-\infty}^{z} V(\rho, z') dz'}.
\]

(2.58)

Therefore after propagating through a thin sample, the wave at the plane \( z \) can be described as

\[
\Psi(\rho, z) = e^{ik_0 r} e^{-i \frac{\hbar v}{\rho} \int_{-\infty}^{z} V(\rho, z') dz'} = e^{ik_0 r} e^{i \Phi(\rho, z)}.
\]

(2.59)

The term

\[
\Phi(\rho, z) = - \frac{1}{\hbar v} \int_{-\infty}^{z} V(\rho, z') dz'
\]

(2.60)

is defined as the projected potential. When \( \Phi(\rho, z) \) is much smaller than 1, Eq. (2.59) is given approximately by

\[
\Psi(\rho, z) \approx e^{ik_0 r} (1 - \frac{i}{\hbar v} \int_{-\infty}^{z} V(\rho, z') dz').
\]

(2.61)

This approximation taken at the exit plane \( z = z_e \) behind the object is the so-called weak phase-object approximation (WPOA), which is in agreement with the first Born
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Next, we are going to verify the optical theorem for the POA. Suppose that the electron wave scattered by a phase object is elastically scattered for a second time, then the total elastic scattering amplitude can be calculated by substituting Eq. (2.59) into Eq. (2.48) for $\Psi_k(r')$:

$$f(k_0, k) = -\frac{me}{2\pi\hbar^2} \int_{-\infty}^{+\infty} e^{-ik_0 r} V(\rho, z) e^{-\frac{i}{\hbar} \int_{-\infty}^{+\infty} V(\rho, z') dz'} dz d^2 \rho. \tag{2.62}$$

Based on Eq. (2.58) we can see that the term $V(\rho, z) e^{-\frac{i}{\hbar} \int_{-\infty}^{+\infty} V(\rho, z') dz'}$ in Eq. (2.62) is proportional to the derivative of $T$ with respect to $z$:

$$\frac{dT}{dz} = -\frac{i}{\hbar v} V(\rho, z) e^{-\frac{i}{\hbar} \int_{-\infty}^{+\infty} V(\rho, z') dz'}. \tag{2.63}$$

Hence we can calculate the integral with respect to $z$ in Eq. (2.62) as

$$\int_{-\infty}^{+\infty} V(\rho, z) e^{-\frac{i}{\hbar} \int_{-\infty}^{+\infty} V(\rho, z') dz'} dz = i\hbar v \int_{-\infty}^{+\infty} \frac{dT}{dz} dz. \tag{2.64}$$

we have $T = 1$ as boundary condition at the limit $z \to -\infty$. Therefore

$$T = e^{-\frac{i}{\hbar v} \int_{-\infty}^{+\infty} V(\rho, z') dz'} - 1 = e^{i\Phi(\rho, \infty)} - 1, \tag{2.65}$$

with $\Phi(\rho, \infty) = -\frac{1}{i\hbar v} \int_{-\infty}^{+\infty} V(\rho, z') dz'$. Eq. (2.62) reduces to

$$f(k_0, k) = -\frac{imev}{2\pi\hbar^2} \int_{-\infty}^{+\infty} e^{-i(k_0 - k_0) r} \left[e^{i\Phi(\rho, \infty)} - 1\right] d^2 \rho. \tag{2.66}$$

Figure 2.3: Vector relation during the elastic scattering process. $k_0$ is the incident wave vector. $k_r$ is the scattered wave vector. $K$ is the scattering vector. $\theta$ is the scattering angle. $\rho$ is a vector lying in the sample plane. $\varphi$ is the angle between $K$ and $\rho$. For small angle scattering ($\theta \to 0$), $K$ is approximately perpendicular to the $z$-axis and parallel to the sample plane, therefore $\varphi$ equals the angle between $\rho$ and the projection of $K$ on the sample plane.

For small angle scattering, we can assume that $k_0 - k_r$ lies perpendicular to $k_0$ (Fig. 2.3). If we decompose the vector $r$ into two components - the in-plane vector $\rho$ and the scalar $z$ lying parallel to $k_0$, then the inner product $(k_0 - k_r) r$ becomes $(k_0 - k_r) r = -K \rho = -K \rho \cos \varphi$. Furthermore, for small angle approximation we obtain $K = 2k_0 \sin \frac{\theta}{2} \approx k_0 \theta$. We replace $\Phi(\rho, \infty)$ with $\Phi(\rho)$ for simplification and write
Eq. (2.66) as

\[ f(k, \mathbf{k}) = f(\theta) = \frac{i m e^v}{2 \pi \hbar} \int_{-\infty}^{+\infty} e^{-i (k_0 - k_0) \rho} \left[ e^{i \Phi(\rho)} - 1 \right] d^2 \rho \]

\[ = \frac{k_0}{2 \pi i} \left[ \int_{-\infty}^{+\infty} i \sin \Phi(\rho) e^{-i K \rho} d^2 \rho - 2 \int_{-\infty}^{+\infty} \sin^2 \frac{\Phi(\rho)}{2} e^{-i K \rho} d^2 \rho \right] \]

\[ = \frac{k_0}{2 \pi i} \left[ \int_{0}^{\infty} i \sin \Phi(\rho) J_0(k_0 \rho \theta) \rho d\rho - 2 \int_{0}^{\infty} \sin^2 \frac{\Phi(\rho)}{2} J_0(k_0 \rho \theta) \rho d\rho \right]. \]

The real and imaginary part of \( f(\theta) \) are

\[ \text{Re} f(\theta) = k_0 \int_{0}^{\infty} \sin \Phi(\rho) J_0(k_0 \rho \theta) \rho d\rho, \]

\[ \text{Im} f(\theta) = 2 k_0 \int_{0}^{\infty} \sin^2 \frac{\Phi(\rho)}{2} J_0(k_0 \rho \theta) \rho d\rho. \]

The scattering cross section based on the POA is

\[ \sigma = \int |f(\theta)|^2 d\Omega = 2 \pi k_0^2 \int_{0}^{\infty} \int_{0}^{\infty} \left[ e^{i \Phi(\rho)} - 1 \right] \left[ e^{-i \Phi(\rho')} - 1 \right] J_0(k_0 \rho \theta) J_0(k_0 \rho' \theta) \sin \theta d\theta \rho \rho' d\rho d\rho' \]

\[ \approx 2 \pi k_0^2 \int_{0}^{\infty} \int_{0}^{\infty} \left[ e^{i \Phi(\rho)} - 1 \right] \left[ e^{-i \Phi(\rho')} - 1 \right] J_0(k_0 \rho \theta) J_0(k_0 \rho' \theta) \delta(\rho - \rho') \rho d\rho d\rho' \]

\[ = 2 \pi \int_{0}^{\infty} \left[ e^{i \Phi(\rho)} - 1 \right] \left[ e^{-i \Phi(\rho')} - 1 \right] \delta(\rho' - \rho) \rho d\rho \]

\[ = 8 \pi \int_{0}^{\infty} \sin^2 \frac{\Phi(\rho)}{2} \rho d\rho \]

\[ = \frac{4 \pi}{k_0} \text{Im} f(0). \]

Here we have employed the property of Bessel function of the first kind and the property of the delta function:

\[ \delta(u - v) = u \int_{0}^{\infty} J_0(ux) J_0(vx) x dx, \]

\[ \delta(ax) = \frac{1}{|a|} \delta(x). \]

We have verified that the POA satisfies the optical theorem, and thus conserves the number of particles. This conclusion indicates that for the image calculation utilizing the POA, the image intensity (the summed intensity of all the image pixels) should be equal to the intensity of the incident electron wave.

### 2.1.5 Multislice method

Multiple scattering caused by the increase of sample thickness is not taken into account by the POA since the three-dimensional sample potential is projected onto a plane and the thickness information gets lost totally. In order to avoid this situation, multislice method offers one solution. Assuming that the interaction between the incident electron beam and the sample is always elastic, then one can solve the final wave equation in the following procedure:
2.2. INELASTIC SCATTERING

1. Slice the sample into layers with the thickness of $\Delta z$ which is within the frame of the POA, $\Delta z < a^2/\lambda$.

2. Project the potential of each layer onto one single slice with infinitely small thickness. Then the distance between the slices becomes $\Delta z$.

3. Propagate the incident wave within each slice based on the POA, and between the slices based on the Fresnel approximation.

The sketch is shown in Fig. 2.4. After propagating through the first slice, the outgoing wave $\psi_1$ equals the incident wave $\psi_0$ multiplied by the transmission function $T_1(\rho,0) = \exp[-\frac{i}{\hbar \omega} \int_{-\infty}^{\infty} V(\rho, z') dz']$, resulting in $\psi_1(\rho,0) = \psi_0 T_1(\rho,0)$. Above the second slice the wave function is expressed as

$$\psi_1(\rho, \Delta z) = \frac{\Delta z}{i \lambda} \int \psi_1(\rho,0) e^{ik_0 r} d^2 \rho'.$$  \hspace{1cm} (2.73)

Here $r = \sqrt{(\rho - \rho')^2 + \Delta z^2}$, where $\rho$ and $\rho'$ are two vectors lying in the first and the second slice, respectively. For the Fresnel approximation, we have $|\rho - \rho'|/\Delta z \ll 1$. Hence expanding $r$ into a Taylor series and only keeping the first two terms, we obtain

$$r = \Delta z \sqrt{1 + \frac{(\rho - \rho')^2}{\Delta z^2}} \approx \Delta z + \frac{(\rho - \rho')^2}{2 \Delta z}.$$  \hspace{1cm} (2.74)

Therefore Eq. (2.73) can be written as

$$\psi_1(\rho, \Delta z) = \frac{e^{ik_0 \Delta z}}{i \lambda \Delta z} \int \psi_1(\rho,0) e^{\frac{ik_0}{\Delta z} (\rho - \rho')^2} d^2 \rho'.$$  \hspace{1cm} (2.75)

If we define

$$P(\rho, \Delta z) = \frac{e^{ik_0 \Delta z}}{i \lambda \Delta z} e^{\frac{ik_0 \rho^2}{4 \pi \Delta z}},$$  \hspace{1cm} (2.76)

then Eq. (2.75) can be expressed as the convolution between $\psi_1(\rho, 0)$ and $P(\rho, \Delta z)$. We can calculate the convolution with the help of Fourier transform. The Fourier transform of $P(\rho, \Delta z)$ is

$$\tilde{P}(q, \Delta z) = FT[P(\rho, \Delta z)] = e^{ik_0 \Delta z} \exp(-i \frac{q^2 \Delta z \lambda}{4 \pi}).$$  \hspace{1cm} (2.77)

The whole propagation process is then described as

$$\psi_n(\rho, z_n) = [\psi_{n-1}(\rho, z_{n-1}) \cdot T_n(\rho, \Delta z)] \otimes P(\rho, \Delta z)$$
$$= FT^{-1}\{FT[\psi_{n-1}(\rho, z_{n-1}) \cdot T_n(\rho, \Delta z)] \cdot \tilde{P}(q, \Delta z)\}.$$  \hspace{1cm} (2.78)

Here $z_n = n \Delta z$ and $T_n$ is the transmission function of the $nth$ layer.

2.2 Inelastic scattering

2.2.1 Basics

At the beginning of Chap. 2 we have reviewed the difference between elastic scattering and inelastic scattering. For inelastic scattering, the incident wave and the excited object states are coupled, therefore one cannot ignore the excitations of the object as
in the case of elastic scattering. Instead of using a pure wave function as in the case of elastic scattering, we express the wave function as the product of the incident wave and the object state (Eq. (2.7)). For the inelastic scattering event involving only one incident electron and one atom as the scatterer, we substitute Eq. (2.7) into Eq. (2.5) and obtain

\[
\begin{align*}
  i\hbar \sum_{j=0}^{\infty} \frac{\partial \Psi_j}{\partial t} & \phi_j e^{-iE_j t/\hbar} + \sum_{j=0}^{\infty} E_j \Psi_j \phi_j e^{-iE_j t/\hbar} = \sum_{j=0}^{\infty} [\hat{H}_A + \hat{H}_B + \hat{W}] \Psi_j \phi_j e^{-iE_j t/\hbar},
\end{align*}
\]

(2.79)

with

\[
\begin{align*}
  \hat{H}_A &= \frac{\hbar^2}{2m_e} \Delta r, \\
  \hat{H}_B &= \sum_{\nu=1}^{Z} \frac{\hbar^2}{2m_e} \Delta r_{e \nu} + \sum_{\mu < \nu} \frac{e^2}{4\pi \epsilon_0} \frac{1}{|r_{\mu} - r_{\nu}|} - \frac{Ze^2}{4\pi \epsilon_0} \frac{1}{|r_{\nu} - R|}, \\
  \hat{W} &= \sum_{\nu=1}^{Z} \frac{e^2}{4\pi \epsilon_0} \frac{1}{|r - r_{\nu}|} - \frac{Ze^2}{4\pi \epsilon_0} \frac{1}{|r - R|}.
\end{align*}
\]

(2.80, 2.81, 2.82)

Here \( r, r_{\nu} \) and \( R \) are the positional vectors of the incident electron, the \( \nu \)th object electron and the atomic nucleus, respectively.

For the object electrons, the following relation holds true

\[
\sum_{j=0}^{\infty} E_j \Psi_j \phi_j e^{-iE_j t/\hbar} = \sum_{j=0}^{\infty} \hat{H}_B \Psi_j \phi_j e^{-iE_j t/\hbar}.
\]

(2.83)
Therefore Eq. (2.79) reduces to
\[ i\hbar \sum_{j=0}^{\infty} \frac{\partial \phi_j}{\partial t} e^{-iE_j t/\hbar} = \sum_{j=0}^{\infty} [\hat{H}_A + \hat{W}] \phi_j e^{-iE_j t/\hbar}. \] (2.84)

Multiplying \( \phi_j^* \) with Eq. (2.84) and integrating both sides over all the coordinates of the electrons in the object, we obtain based on Eq. (2.9):
\[ i\hbar \sum_{j=0}^{\infty} \frac{\partial \Psi_j}{\partial t} \langle m|j \rangle = \sum_{j=0}^{\infty} [\hat{H}_A \langle m|j \rangle + \langle m|\hat{W}|j \rangle] \Psi_j, \] (2.85)
which leads to
\[ i\hbar \frac{\partial}{\partial t} \Psi_j(r,t) = -\frac{\hbar^2}{2m_e} \Delta r \Psi_j(r,t) + V_{mj} \Psi_j(r,t). \] (2.86)

Here \( V_{mj} \) is a transition matrix defined as
\[ V_{mj} = \langle m|\hat{W}|j \rangle. \] (2.87)

We can introduce the the scattering amplitude \( f(k_j, k_0) \) and write Eq. (2.7) in this form:
\[ \psi_t = e^{ik_0 r} |0\rangle + \sum_{j=0}^{\infty} f_j(k_j, k_0) e^{ik_j r} |j\rangle. \] (2.88)

Eq. (2.88) resembles Eq. (2.13). The calculation of the first order scattering amplitude \( f_j(k_j, k_0) \) is similar to the case of elastic scattering and the detailed derivation can be found in [73]. We obtain the first-order scattering amplitude as
\[ f(k_j, k_0) = -\frac{m_e}{2\pi\hbar^2} (k_j, j|\hat{W}|k_0, 0) = -\frac{m_e}{2\pi\hbar^2} (k_j|V_{j0}|k_0). \] (2.89)

Here \( V_{j0} \) is the transition matrix
\[ V_{j0} = \langle j|\hat{W}|0\rangle. \] (2.90)

Correspondingly, the scattering cross section \( \sigma \) and the differential scattering cross section \( d\sigma/d\Omega \) can be derived similar to Sec. 2.1.1. The current density is calculated from Eq. (2.7) and the incoming current density is the same as Eq. (2.15). Utilizing the orthonormal relation (Eq. (2.9)), we obtain the outgoing current density
\[ j_e = \frac{\hbar}{2m_e} \sum_{j=0}^{\infty} (\Psi_j \nabla \Psi_j^* - \Psi_j^* \nabla \Psi_j) = \frac{\hbar}{m_e} Im \sum_{j=0}^{\infty} \Psi_j \nabla \Psi_j^*. \] (2.91)

With the same geometry in Fig. 2.1, we integrate the incoming and the outgoing current
density over the area $\sigma$ and $S$, respectively, which results in
\[
\sigma = \int \sum_{j=0}^{\infty} \frac{k_j}{k_0} |f(k_j, k_0)|^2 d\Omega, \tag{2.92}
\]
\[
d\sigma = \sum_{j=0}^{\infty} \frac{k_j}{k_0} |f(k_j, k_0)|^2 d\Omega, \tag{2.93}
\]

The case $j = 0$ corresponds to elastic scattering at the ground state of the object.

In Sec. 2.1.2 we have derived the optical theorem for elastic scattering. Similarly, this theorem can be extended to inelastic scattering. Our assumption is that during the scattering, the total number of electrons in the whole system is a constant, indicating that the wave function of the whole system (Eq. (2.7)) satisfies \( \partial (\psi^*_t \psi_t) / \partial t = 0 \). On the analogy of Eq. (2.31) we obtain
\[
\iint (\psi_t \nabla \psi^*_t - \psi^*_t \nabla \psi_t) \cdot n_S dS = 0. \tag{2.94}
\]

Substituting Eq. (2.88) into Eq. (2.94) and based on the relation of completeness (Eq. (2.10)) and orthonormality (Eq. (2.9)), we obtain
\[
\iint (\psi_t \nabla \psi^*_t - \psi^*_t \nabla \psi_t) \cdot n_S dS = \iint (\psi_0 \nabla \psi^*_0 - \psi^*_0 \nabla \psi_0) \cdot n_S dS + \iint (\psi_e \nabla \psi^*_e - \psi^*_e \nabla \psi_e) \cdot n_S dS + \iint (\psi^*_0 \nabla \psi^*_e - \psi^*_e \nabla \psi^*_0) \cdot n_S dS + \sum_{j=1}^{\infty} \iint (\psi_j \nabla \psi^*_j - \psi^*_j \nabla \psi_j) \cdot n_S dS = 0. \tag{2.95}
\]

Here \( \psi_0 \) and \( \psi_e \) are defined by Eqs. (2.11) and (2.12), respectively. \( \Psi_j \) is defined as
\[
\Psi_j = f_j(k_j, k_0) e^{ik_j r} \quad (j \geq 1). \tag{2.96}
\]

The first four terms in Eq. (2.95) have been calculated in Sec. 2.1.2 and the sum results in \(-2ik_0 \sigma_{el} + 8\pi i \text{Im} f(0)\). Here \( \sigma_{el} \) is defined as the elastic scattering cross section. The last term can be obtained on the analogy of Eq. (2.36) as
\[
\sum_{j=1}^{\infty} \iint (\Psi_j \nabla \Psi^*_j - \Psi^*_j \nabla \Psi_j) = -2i \sum_{j=1}^{\infty} k_j |f_j(k_j, k_0)|^2 d\Omega = -2i k_0 \sum_{j=1}^{\infty} \int k_j |f_j(k_j, k_0)|^2 d\Omega = -2ik_0 \sigma_{in}. \tag{2.97}
\]

Here \( \sigma_{in} \) is defined as the inelastic scattering cross section. The relation in Eq. (2.95) finally leads to
\[
\frac{4\pi}{k_0} \text{Im} f(0) = \sigma_{el} + \sigma_{in} = \sigma_t. \tag{2.98}
\]
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Here \( \sigma_t \) denotes the total scattering cross section.

The optical theorem (Eq. (2.98)) generalized for both elastic and inelastic scattering has important applications in experiments as well as in image calculations involving mixed elastic and inelastic scattering. According to this theorem, the total image intensity, contributed by both the elastically and inelastically scattered waves, is equal to the intensity of the incident electron wave. One can use an energy filter to select the imaging electrons of a required energy, and based on the filtered image intensity the number of the electrons with this specific energy as well as its corresponding scattering cross section can be estimated.

2.2.2 Coherence and incoherence

Waves are coherent if there is a fixed phase relation between them. The coherent waves can interfere with each other and the wave functions can be superposed. When there is no fixed phase relation between the waves, there is no interference and only the intensities of the waves can be summed up. In the latter case, the waves are incoherent.

The observable intensity of the system in Eq. (2.7) can be written as:

\[
\langle \psi_t | \psi_t \rangle = \left( \sum_{m=0}^{\infty} \langle m | \Psi_m^* \rangle \sum_{j=0}^{\infty} \Psi_j \langle j \rangle \right) = \sum_{m,j} \Psi_m^* \Psi_j \delta_{m,j} = \sum_{j=1}^{\infty} |\Psi_j|^2 = \sum_{j=0}^{\infty} |\Psi_j|^2 + |\psi_0 + \psi_e|^2. \tag{2.99}
\]

The total intensity is contributed by the intensity of each scattered partial wave corresponding to a specific object eigenstate, therefore the scattered waves are incoherent with each other as long as the coupled object states are different. The second term in Eq. (2.99) implies that the elastically scattered wave \( \psi_e \) and the non-scattered wave \( \psi_0 \) are coherent with each other since the waves can be superposed.

For inelastic scattering, we can not describe the propagation of the wave with a pure wave function as in the case of elastic scattering, since inelastic waves are coupled with the excited object states. Rose was inspired by the concept of mutual coherence function (MCF) applied in optics \[78\], and extended its usage to the handling of the wave propagation in the electron microscope \[55\]. Mutual coherence function accounts for the spatial and temporal interference between the waves which correspond to the same object state. Unlike the pure wave function, the propagation of the MCF denoted by \( \Gamma \) preserves the amplitude and phase resulting from wave interference. \( \Gamma \) is expressed as

\[
\Gamma = \langle \Psi^*(r',t) \Psi(r,t-\tau) \rangle. \tag{2.100}
\]

Here \( \tau \) is the temporal difference between the two waves, and \( r' \) and \( r \) indicate that the two waves originate from different sources. The brackets represent the time average.

2.2.3 Mixed dynamic form factor (MDFF)

The elastic form factor of a single atom can be described as the Fourier transform of its electron density at the ground state \( |0\rangle \). For a single atom with the atomic number \( Z \),
we introduce the density operator
\[ \hat{n}(K) = \sum_{\nu=1}^{Z} \hat{n}_\nu(K) = \sum_{\nu=1}^{Z} e^{-iK\hat{r}_\nu}. \] (2.101)

and write the elastic form factor of the atom as
\[ F(K) = \langle 0|\hat{n}(K)|0 \rangle = \sum_{\nu=1}^{Z} \langle 0|\hat{n}_\nu(K)|0 \rangle = \sum_{\nu=1}^{Z} e^{-iK\hat{r}_\nu}|0\rangle. \] (2.102)

For inelastic scattering, the \text{MDFF} is expressed as \[ \text{55} \]
\[ S(K, K', E) = \sum_{j=1}^{\infty} \langle 0|\hat{n}(K)|j \rangle \langle j|\hat{n}(-K')|0 \rangle \delta(E - E_j + E_0). \] (2.103)

Here \( E_0 \) and \( E_j \) are the energies corresponding to the ground state \(|0\rangle\) and the excited state \(|j\rangle\) of the object, respectively. For a many-body system, the eigenstate of the object is an ensemble of all the particle states. For a single atom, if we neglect the interactions between the electrons in the atom, then the \text{MDFF} can be expressed utilizing the eigenstates of single electrons, derived with the help of a Slater determinant \[ \text{79} \]. We obtain
\[ S(K, K', E) = \sum_{\nu=1}^{Z} \sum_{\mu=Z+1}^{\infty} \langle \phi_{\nu}|e^{-iK\hat{r}_\nu}|\phi_{\mu} \rangle \langle \phi_{\mu}|e^{iK'\hat{r}}|\phi_{\nu} \rangle \delta(E - E_\mu + E_\nu). \] (2.104)

Here \( \phi_{\nu} \) is an occupied state and the total number of the occupied states equals the number of electrons in the atom. \( \phi_{\mu} \) is an empty state. An electron at the initial occupied state \( \phi_{\nu} \) can only be excited to an empty state \( \phi_{\mu} \). Because according to Pauli exclusion principle, each quantum state can hold only one electron. All occupied states and all empty states form a complete set:
\[ I = \sum_{\nu=1}^{Z} |\phi_{\nu}\rangle \langle \phi_{\nu}| + \sum_{\mu=Z+1}^{\infty} |\phi_{\mu}\rangle \langle \phi_{\mu}|. \] (2.105)

Assuming the average energy loss \( \Delta E = E_\mu - E_\nu \) and with the help of Eq. \[ \text{2.105} \], we can write Eq. \[ 2.104 \] as
\[ S(K, K', E) = \delta(E - \Delta E) \sum_{\nu=1}^{Z} \langle \phi_{\nu}|e^{-i(K-K')\hat{r}}|\phi_{\nu} \rangle - \sum_{\nu=1}^{Z} \sum_{\nu'=1}^{Z} \langle \phi_{\nu}|e^{-iK\hat{r}}|\phi_{\nu'} \rangle \langle \phi_{\nu'}|e^{iK'\hat{r}}|\phi_{\nu} \rangle. \] (2.106)

The second term in Eq. \[ 2.106 \] can be written as
\[ \sum_{\nu=1}^{Z} \sum_{\nu'=1}^{Z} \langle \phi_{\nu}|e^{-iK\hat{r}}|\phi_{\nu'} \rangle \langle \phi_{\nu'}|e^{iK'\hat{r}}|\phi_{\nu} \rangle = \sum_{\nu=1}^{Z} \sum_{\nu'=1}^{Z} \int \phi_{\nu}^*(r)\phi_{\nu'}(r)\phi_{\nu'}^*(r')\phi_{\nu}(r')e^{-iK\hat{r}}e^{iK'\hat{r}'}drdr'. \] (2.107)
2.2. INELASTIC SCATTERING

Defining the mixed electron density \( n(r, r') \)

\[
n(r, r') = \sum_{\nu=1}^{Z} \phi_{\nu}^*(r)\phi_{\nu}(r')
\]  

(2.108)

and the pure electron density \( n(r) \)

\[
n(r) = \sum_{\nu=1}^{Z} \phi_{\nu}^*(r)\phi_{\nu}(r),
\]  

(2.109)

we obtain the relations:

\[
\hat{n}(r)dr = \sum_{\nu=1}^{Z} \hat{\phi}_{\nu}^*(r)\hat{\phi}_{\nu}(r)dr = Z, 
\]  

(2.110)

\[
\hat{|n(r, r')|^2}drdr' = \frac{1}{Z} \int n(r)dr \int n(r')dr' = Z. 
\]  

(2.112)

We approximate

\[
|n(r, r')|^2 \approx \frac{1}{Z} n(r)n(r'), 
\]  

(2.113)

and Eq. (2.106) becomes

\[
S(K, K', E) \approx \delta(E - \Delta E)[F(K - K') - \int \frac{1}{Z} n(r)n(r')e^{-iK'r}dr'dr'] 
\]  

\[= \delta(E - \Delta E)[F(K - K') - \frac{1}{Z} F(K)F(-K')].
\]  

(2.114)

The MDFF in the form of Eq. (2.114) is defined as the Raman-Compton approximation for a single atom. In the case of \( K = K' \), we obtain

\[
S(K, E) = \delta(E - \Delta E)[Z - \frac{1}{Z}|F(K)|^2].
\]  

(2.115)

The advantage of Eq. (2.114) is to allow to account for inelastic scattering by the elastic form factor of a single atom. For a multi-atom system, if the interactions between the atoms can be neglected, then the MDFF can be expressed accordingly as

\[
S(K, K', \Delta E) = p(\Delta E) \sum_{\nu} e^{-i(K - K')\rho_{\nu}}[F_{\nu}(K - K') - \frac{1}{Z_{\nu}} F_{\nu}(K)F_{\nu}(K')].
\]  

(2.116)

Here \( Z_{\nu}, \rho_{\nu} \) and \( F_{\nu} \) are the atomic number, the positional vector and the elastic form factor of the \( \nu \)th atom, respectively. \( p(\Delta E) \) represents the average energy distribution of the whole system.
2.2.4 Mutual object transparency (MOT)

In order to generalize the scattering of the incident wave in a thin object, the concept of MOT is introduced as \[\gamma(\rho, \rho', \tau) = \langle e^{i\Phi(\rho, t)} e^{-i\Phi(\rho', t - \tau)} \rangle,\] (2.117)

where \(\tau\) accounts for the temporal interference between two points \(\rho\) and \(\rho'\) on the object. The brackets represent the time average. The MOT is an extension of the POA (Sec. 2.1.4). The POA is applied modeling the elastic scattering of a pure electron wave in a thin object, while the MOT accounts for both the elastic and inelastic scattering of an MCF in a thin object.

The Taylor expansion of MOT (Eq. (2.117)) to the second order of \(\Phi\) results in Eq. (2.118) \[\gamma(\rho, \rho', \tau) \approx \exp\left[i\mu_1(\rho) - i\mu_1(\rho') - \frac{1}{2}\mu_2(\rho) - \frac{1}{2}\mu_2(\rho') + \mu_{11}(\rho, \rho', \tau)\right],\] (2.118)

with the definitions

\[\mu_1(\rho) = \langle \Phi(\rho, t) \rangle,\]

\[\mu_{11}(\rho, \rho', \tau) = \langle \Phi(\rho, t)\Phi(\rho', t - \tau) \rangle - \langle \Phi(\rho, t) \rangle \langle \Phi(\rho', t - \tau) \rangle\]

\[= \sum_{j \neq m} P_m e^{i\omega_m \tau} \langle m | \Phi(\rho') | j \rangle \langle j | \Phi(\rho) | m \rangle\] (2.120)

\[\mu_2(\rho) \approx \langle \Phi^2(\rho, t) \rangle - \langle \Phi(\rho, t) \rangle^2 = \mu_{11}(\rho = \rho', \tau = 0).\] (2.121)

The function \(\mu_1\) represents the static projected potential. The variable \(\mu_2\) is related to the variable \(\mu_{11}\) by Eq. (2.121). \(\mu_2\) is independent of the time and works in the exponent like an absorption factor, which accounts for the decrease of the intensity of the outgoing MCF caused by the reduction of the purely elastically scattered electrons. The factor \(\mu_{11}\) accounts for the increase of the intensity of the outgoing MCF contributed by the inelastically scattered electrons.

At the end of Sec. 2.2.1, we have proved the generalized optical theorem for both elastic and inelastic scattering. Like the POA (Sec. 2.1.4), the MOT Eq. (2.118) satisfies the optical theorem, indicating that the total number of electrons is conserved during the scattering process:

\[\gamma(\rho = \rho', \tau = 0) = 1.\] (2.122)

In the following text, we are going to explore the relation between the MDFF and the term \(\mu_{11}\). For fast electrons, the matrix element \(\langle j | \Phi | m \rangle\) in Eq. (2.120) is given by

\[\langle j | \Phi | m \rangle = -\frac{1}{\hbar v} \int_{-\infty}^{+\infty} V_{jm} dz.\] (2.123)

Here \(V_{jm} = \langle j | \hat{W} | m \rangle\) and the operator \(\hat{W}\) is defined by Eq. (2.82). We obtain

\[V_{jm} = \langle j | \hat{W} | m \rangle = \sum_{\nu=1}^{Z} \langle j | e^{2} \frac{1}{4\pi\epsilon_0} \frac{1}{|r - r_{\nu}|} | m \rangle - \langle j | \frac{Ze^{2}}{4\pi\epsilon_0} \frac{1}{|r - R|} | m \rangle.\] (2.124)
In the second term of Eq. 2.124, \(|j\rangle|m\rangle\) are the eigenstates of the object electron, which are not related to the Coulomb interaction between the incident electron and the nucleus. Since \(j \neq m\), we obtain

\[
\langle j | \frac{Ze^2}{4\pi\varepsilon_0} \frac{1}{|r-R|} |m\rangle = \langle j|m\rangle \frac{Ze^2}{4\pi\varepsilon_0} \frac{1}{|r-R|} = 0.
\]

By introducing the Sommerfeld constant \(\alpha_s = e^2/(4\pi\varepsilon_0 hc)\) and the relative velocity \(\beta = v/c\) with \(c\) the velocity of the light, we can write the first term in Eq. 2.124 as

\[
\sum_{\nu=1}^{Z} \langle j | \frac{e^2}{4\pi\varepsilon_0} \frac{1}{|r-r_\nu'|} |m\rangle = \sum_{\nu=1}^{Z} \langle j | \alpha_s \frac{hc}{|r-r_\nu'|} |m\rangle,
\]

and \(\mu_{11}\) (Eq. 2.120) as

\[
\mu_{11}(\rho, \rho', \tau) = \left(\frac{\alpha_s}{\beta}\right)^2 \int \int \sum_{\nu=1}^{Z} \sum_{j \neq m} \sum_{\nu'=1}^{Z} e^{i\omega_{j\nu} \tau} (|m\rangle \frac{1}{|r-r_\nu'|} \langle j | |j\rangle \frac{1}{|r-r_\nu'|} |m\rangle) dz dz'.
\]

Defining the Fourier transform with respect to \(r\) and inverse Fourier transform with respect to \(r'\):

\[
M_{jm}^{(v)}(K) = FT[|j| \frac{1}{|r-r_\nu'|} |m\rangle],
\]

\[
M_{mj}^{(v')} (K') = FT^{-1}[|m\rangle \frac{1}{|r'-r_\nu'|} |j\rangle],
\]

respectively, we can transform Eq. 2.127 into

\[
\mu_{11}(\rho, \rho', \tau) = \left(\frac{\alpha_s}{4\pi^2\beta}\right)^2 \int \int \sum_{\nu=1}^{Z} \sum_{j \neq m} \sum_{\nu'=1}^{Z} e^{i\omega_{jm} \tau} M_{mj}^{(v')} (K') M_{jm}^{(v)} (K) e^{iKr_\rho e^{-iK_r'}} d^3K r d^3K' r'.
\]

Here \(K_\rho\) and \(K'_r\) indicate that the Fourier transforms in Eq. 2.130 are performed with respect to the plane containing \(\rho\) and the one containing \(\rho'\). By introducing \(r'' = r - r_\nu\), we calculate \(M_{jm}^{(v')}\) as follows:

\[
M_{jm}^{(v)}(K) = FT[|j| \frac{1}{|r-r_\nu'|} |m\rangle]
\]

\[
= \int_{-\infty}^{+\infty} \phi_j^* (r_\nu) \phi_m (r_\nu) \frac{1}{|r-r_\nu'|} e^{-iKr_\nu} d^3r d^3r_\nu
\]

\[
= \int_{-\infty}^{+\infty} \frac{1}{r''} e^{-iKr''} d^3r'' \int_{-\infty}^{+\infty} \phi_j^* (r_\nu) \phi_m (r_\nu) e^{-iK_r'} d^3r_\nu.
\]

The first integral over the whole space results in \(4\pi/K^2\), therefore Eq. 2.131 becomes

\[
M_{jm}^{(v)}(K) = \frac{4\pi}{K^2} \int_{-\infty}^{+\infty} \phi_j^* (r_\nu) \phi_m (r_\nu) e^{-iKr_\nu} d^3r_\nu = \frac{4\pi}{K^2} \langle j | e^{-iKr_\nu} |m\rangle.
\]
Similarly, we obtain

\[ M^{(\nu')}_{mn}(K') = \frac{4\pi}{K'^2} \langle m|e^{i\mathbf{K}'r'}|j\rangle. \]  

(2.133)

We suppose that the initial state of the object is the ground state: \(|m\rangle = |0\rangle\). Then substituting Eqs. (2.132) and (2.133) into Eq. (2.130), we obtain

\[ \sum_{\nu=1}^{Z} \sum_{\nu'=1}^{Z} \sum_{j \neq m} e^{i\omega_{\nu}\tau} M^{(\nu')}_{m\nu}(K')M^{(\nu)}_{m\nu}(K) = \frac{16\pi^2}{K^2K'^2} \sum_{\nu=1}^{Z} \sum_{\nu'=1}^{Z} \sum_{j=1}^{\infty} e^{i\omega_{\nu}\tau} \langle 0|e^{i\mathbf{K}'r'}|j\rangle \langle j|e^{-i\mathbf{K}r_{\nu}}|0\rangle \]  

(2.134)

\[ = \frac{16\pi^2}{K^2K'^2} \sum_{j=1}^{\infty} e^{i\omega\tau} \langle 0|\hat{n}(\mathbf{K}'|j\rangle \langle j|\hat{n}(\mathbf{-K})|0\rangle \delta(\omega - \omega_j + \omega_0) \]  

\[ = \frac{16\pi^2}{K^2K'^2} \int e^{i\omega\tau} S(K, K', \omega) d\omega. \]

We assume that the distribution of the energy loss \(\Delta E = \hbar\omega\) is quasi-continuous, therefore the sum over all the excited object states in the third row of Eq. (2.134) can be written as the integral about \(\omega\). Substituting Eqs. (2.134) into Eq. (2.130), we end up with

\[ \mu_{11}(\rho, \rho', \tau) = \left(\frac{\alpha_s}{\pi\beta}\right)^2 \int \int e^{i\omega\tau} \frac{S(K, K', \omega)}{K^2K'^2} e^{i\mathbf{K}\rho} e^{-i\mathbf{K}'\rho'} d\omega d\mathbf{K} d\mathbf{K}' d\mathbf{\rho} d\mathbf{\rho}', \]  

(2.135)

which connects the MDFF and the term \(\mu_{11}\). For our image calculation, the MOT accounts for the simultaneous elastic and inelastic scattering in a thin object. In order to calculate the MOT, it is crucial to know the factor \(\mu_{11}\) and \(\mu_2\) first, which are related to the MDFF by a four-dimensional Fourier transform in our case (Eq. (2.135)). Four-dimensional Fourier transform is computationally time-consuming. Therefore the main concern in our image calculation is to factorize the 4D Fourier transform as combinations of 2D Fourier transforms.

### 2.2.5 Multislice method

In our image calculation involving both elastic and inelastic scattering, multiple elastic scattering events and one inelastic scattering event are taken into account. The sample is sliced into a number of layers, and the probability of inelastic scattering taking place at each layer is the same, therefore the result should be a statistic average. If the inelastic scattering takes place at the \(n^{th}\) layer, then above as well as below the \(n^{th}\) layer, the propagation of the mutual coherence function \(\Gamma\) is always assumed to be elastic. The procedure follows the order:

1. Input the initial mutual coherence function: \(\Gamma_0(\rho, \rho') = \psi_0(\rho)|\psi_0^*(\rho')\). In the case of coherent axial illumination, \(\psi_0\) is a plane wave.

2. Propagate \(\Gamma_0\) through the first \(n - 1\) layers. If inelastic scattering takes place at the first layer, this step can be skipped.

\[ \Gamma_{n-1}(\rho, \rho') = [\Gamma_{n-2}(\rho, \rho') \cdot T_{n-1}T_{n-1}^*] \otimes P. \]  

(2.136)
Here $TT^*$ is the transmission function adopting the form

$$TT^* = e^{i\Phi(\rho) - \frac{1}{2}\mu_2(\rho)e^{i\Phi(\rho')} - \frac{1}{2}\mu_2(\rho')}.$$  

(2.137)

and $P$ is the Fresnel propagator. The computation of convolution is usually converted into a product of Fourier transforms, where the Fresnel propagator adopts the form:

$$P(q, q') = \exp\left[-i\left(q^2 - q'^2\right)\Delta z \lambda / (4\pi)\right]$$  

(2.138)

with $\Delta z$ the slice thickness and $\lambda$ the wave length of the incident electron wave.

3. Inelastic scattering at the $n^{th}$ layer. The MOT function $\gamma$ (Eq. (2.118)) is further approximated as shown in Eq. (2.139).

$$\Gamma_n(\rho, \rho', \Delta E) = \Gamma_{n-1}(\rho, \rho')\gamma_n(\rho, \rho', \Delta E)$$

$$\approx \Gamma_{n-1}(\rho, \rho')e^{i\Phi(\rho) - \frac{1}{2}\mu_2(\rho)e^{-i(\Phi') - \frac{1}{2}\mu_2(\rho') - b_0 + b_1 \cdot \mu_{11}(\rho, \rho', \Delta E)]}.$$

(2.139)

Here the constant coefficients $b_0$ and $b_1$ are determined by the linear fitting of $e^x$ in the vicinity of $\langle x \rangle$, which satisfies $e^x \approx b_0 + b_1 \cdot x$. In the $n^{th}$ layer, one elastic scattering takes place, denoted by the constant $b_0$ in Eq. (2.139) and one inelastic scattering takes place, denoted by $b_1 \mu_{11}$. The mutual object transparency $\gamma_n(\rho, \rho', \Delta E)$ is related to $\gamma_n(\rho, \rho', \tau)$ in Eq. (2.118) by a Fourier transform:

$$\gamma_n(\rho, \rho', \Delta E) = \int \gamma_n(\rho, \rho', \tau)e^{-i\Delta E\tau / \hbar}d\tau.$$

(2.140)

4. Propagate $\Gamma_n$ elastically through the remaining layers, similar to Step 2. If inelastic scattering takes place at the last layer, this step can be skipped.

The general multislice procedure is summarized in Fig. 2.5. Case A denotes pure elastic scattering with absorption, corresponding to the constant $b_0$ in Eq. (2.139). Case B denotes the inelastic scattering event at the $n^{th}$ layer, corresponding to the term $b_1 \mu_{11}$ in Eq. (2.139). Above and below this layer the propagation is always elastic.

The first step of the image calculation involving mixed elastic/inelastic scattering is to compute the MDFF (Fig. 2.6). The MDFF is expressed in the form of the elastic form factors of single atoms (Eq. (2.116)). Here we utilize the Wentzel model [76] (Appendix B) for the calculation of the elastic form factor $F(K)$:

$$F(K) = \frac{Z}{1 + K^2a^2},$$

(2.141)

where $a = a_HZ^{-1/3}$ is the screening radius in the Wentzel potential and $a_H = 0.0529$ nm is the Bohr radius. In the case of axial plane-wave illumination, the scattering angle equals the aperture angle $\theta$. Assuming in addition small energy loss $\Delta E \ll E_0$, we obtain according to Fig. 2.7:

$$K^2 \approx k_0^2(\theta_E^2 + \theta^2).$$

(2.142)

Here $k_0$ is the incident wave number and
CHAPTER 2. THEORY OF ELECTRON SCATTERING

Figure 2.5: The multislice algorithm involves two different cases - A. Pure elastic propagation of the incident MCF with absorption in the \( n^{th} \) layer, resulting in 1 term; B. Elastic propagation above and below the \( n^{th} \) layer with one inelastic scattering in the \( n^{th} \) layer, resulting in the number of \( k \) terms. Reproduced from Ultramicroscopy with the reference [75].

\[
\theta_E = \frac{\Delta E}{\beta^2 (E_0 + m_e c^2)} \quad (2.143)
\]

is the characteristic inelastic scattering angle with the energy loss \( \Delta E \), the energy of the incident electron \( E_0 \) and the electron mass \( m_e \). For silicon atom at 20 kV with an energy loss of 16 eV, \( \theta_E \) equals 0.4 mrad; and the characteristic elastic scattering angle defined by \( \theta_A = 1/(k_0 a) \) is 62 mrad. This shows that for small energy loss, the characteristic inelastic scattering angle \( \theta_E \) is negligibly small compared with the characteristic elastic scattering angle \( \theta_A \). Writing Eq. (2.141) as

\[
F(\theta) = \frac{Z \theta_A^2}{\theta_A^2 + \theta_E^2 + \theta^2} \quad (2.144)
\]
2.3. SUMMARY

Figure 2.7: The vector relation for inelastic scattering. \( k_0 \) is the incident wave vector; \( k \) is the scattered wave vector; \( K \) is the scattering vector. The projection of \( K \) on the direction of \( k_0 \) equals the product of \( k_0 \) and the characteristic inelastic scattering angle \( \theta_E \).

and substituting Eq. (2.144) for \( F_\nu \) in Eq. (2.116), we obtain

\[
S(K, K', \Delta E) = \sum_\nu e^{-ik(\theta - \theta')\rho_\nu} Z_\nu \frac{\theta_A^2}{\theta_A^2 + (\theta - \theta')^2} - \frac{\theta_E^2}{\theta_E^2 + \theta'^2} \theta_E^2 + \theta_E^2 + \theta^2].
\]

Here \( \theta_A \nu \) is the characteristic elastic scattering angle of the \( \nu \)th atom. The variable \( |\theta - \theta'| \) in the first term acts as a ‘mixed’ cut-off angle, which guarantees that \( \mu_2 \) and \( \mu_{11} \) stay finite for the entire range \( \rho \in [0, \infty] \) (Eqs. (2.135) and (2.121)). Based on Eq. (2.145), all other terms in the brackets are either the function of \( \theta \) or \( \theta' \) except for the first term. If it is possible to write the first term as a combination of the functions depending on \( \theta \) and \( \theta' \) separately, then the MDFF can be written as

\[
S(\theta, \theta', \Delta E) \approx p(\Delta E) \sum_\nu e^{-ik(\theta - \theta')\rho_\nu} Z_\nu \tilde{g}_j(\theta) \tilde{g}_j(\theta').
\]

Here \( \tilde{g}_j(\theta) \) and \( \tilde{g}_j(\theta') \) are the factorized functions for the \( \nu \)th atom with respect to \( \theta \) and \( \theta' \), respectively. The 4D Fourier transform can thus be turned into the combinations of independent 2D Fourier transforms. Correspondingly, according to Eq. (2.145), \( \mu_{11} \) can also be written as a combination of functions depending on \( \rho \) and \( \rho' \), respectively.

In Appendix D a new method for factorizing \( S(\theta, \theta', \Delta E) \) is introduced, and in Chap. 7 this new approximation is applied for image calculations.

Based on Eqs. (2.121) and (2.135) one can derive

\[
\mu_2(\rho) = \int \mu_{11}(\rho = \rho', \Delta E) d(\Delta E).
\]

The energy distribution function \( p(\Delta E) \) is included in the term \( \mu_{11}(\rho = \rho', \Delta E) \).

2.3 Summary

As a summary, the concepts and procedures for image calculations involving elastic and inelastic scattering are listed in Table 2.1.
### Table 2.1: The concepts and procedures for image calculations involving mixed elastic and inelastic scattering as well as pure elastic scattering.

<table>
<thead>
<tr>
<th></th>
<th>Pure Elastic</th>
<th>Elastic/Inelastic</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Incoming</strong></td>
<td>$\psi_0(r)$</td>
<td>$\Gamma_0 = \langle \psi_0^*(r')\psi_0(r) \rangle$ (MCF)</td>
</tr>
<tr>
<td><strong>Object slice</strong></td>
<td>$e^{i\Phi(\rho)}$ (POA)</td>
<td>$\gamma = \langle e^{i\Phi(\rho,t)}e^{-i\Phi(\rho,t-\tau)} \rangle$ (MOT)</td>
</tr>
<tr>
<td><strong>Outgoing</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single slice</td>
<td>$\Psi_0 = \psi_0 e^{i\Phi(\rho)}$</td>
<td>$\Gamma_\epsilon = \Gamma_0 \gamma$ (MCF)</td>
</tr>
<tr>
<td>Multislice</td>
<td>Eq. (2.78)</td>
<td>Eqs. (2.136) and (2.139)</td>
</tr>
</tbody>
</table>
Chapter 3

Imaging process

A transmission electron microscope consists of three parts: the illumination system, the specimen stage and the imaging system. The illumination system is composed of the electron gun and a set of condenser lenses, which shape the electron beam to the required size, convergence and intensity. The specimen stage holds the specimen either stationary or allows the specimen to tilt with certain degree of freedom. The imaging system consists of the strongest lens - the objective lens located below the specimen, the intermediate lens and the projector lens system, which together produce a magnified image or diffraction pattern on the fluorescent screen or the CCD camera.

The propagation process of a monochromatic and highly collimated scattered or un-scattered electron wave through the imaging system can be described by the convolution between the exit-wave function (pure elastic scattering, see Sec. 2.1) or the mutual coherence function (MCF) (mixed elastic and inelastic scattering, see Sec. 2.2) and the transfer function of the optical system, which includes the aberration transfer function of the objective lens (Sec. 3.1), the image spread function (Sec. 3.2), the focus spread function (Sec. 3.2) and the aperture function. The partial temporal coherence of the source as well as the exit-wave/exit-MCF is accounted for by incoherently summing up the images obtained for each monochromatic partial wave. Similarly, the spatial coherence of the source is accounted for by summing up the image obtained for each illumination angle.

However, the influence of the spatial incoherence of the source is ignored in this work. The experiments within the frame of the SALVE project are performed on the FEI Titan Microscope and the SALVE microscopes (SALVE I and SALVE II) based on Zeiss LIBRA 200 MC TEM. FEI Titan is equipped with a Schottky-field emission gun providing an effective source size as small as 0.01 µm and the convergence angle can be as small as 0.5 mrad. SALVE I and SALVE II machines are equipped with Schottky-field emission guns as well as the Titan microscope, however in addition with a monochromator located between the gun and the accelerator. The resulting convergence angle of the beam is as small as 0.2 mrad. In both cases, the beam can be assumed as highly collimated.

In most cases, TEM images are recorded using charge-coupled detectors (CCD) with fiber-optics coupled scintillator. In the ideal case, each electron is only detected by one of the detector pixels. The number of detected electrons varies from pixel to pixel, resulting in different gray levels. In practice, a single imaging electron can cause signals in more than one pixel because of multiple scattering within the scintillator material.
and the creation of an excitation volume. This effect is described by the point-spread function (PSF) of the detector, and its Fourier transform is the modulation-transfer function (MTF) \[80\] \[82\].

In order to include all the effects discussed above in a single imaging model, we extend the existing one introduced in \[49\] by accounting for the partial temporal coherence through incoherently summing up the images obtained for different energies, and including the extra image spread function, focus spread function as well as the MTF of the camera.

For imaging with pure elastically scattered wave, the imaging process is described as

\[
\hat{\Psi}_0(q) = \int \Psi_0(\rho) e^{-iq\rho} d^2\rho, \tag{3.1}
\]

\[
\hat{I}_i(q) = \int \hat{\Psi}_0(q') \hat{\Psi}_0^*(q' + q) e^{-i\chi(q', \Delta E)} e^{i\chi(q' + q, \Delta E)} A(q') A(q' + q) E_{is}(q', q' + q) p(\Delta E) d^2q' d\Delta E, \tag{3.2}
\]

\[
I(\rho) = \int \hat{I}_i(q) MTF(q) e^{i\rho d^2q}. \tag{3.3}
\]

Here \(\Psi_0(\rho)\) denotes the exit-wave; \(e^{-i\chi(q, \Delta E)}\) is the aberration transfer function and \(\Psi(q, \Delta E)\) is the monochromatic image wave in reciprocal space with the energy \(E_0 + \Delta E\). \(E_{is}, E_{fs}\) and \(MTF(q)\) are the image spread function, the focus spread function and the MTF of the camera, respectively. \(A(q)\) is the aperture function which mimics the objective aperture. The partial temporal incoherence of the electron beam is taken into account by the energy distribution function \(p(\Delta E)\). \(\hat{I}_i(q)\) and \(I(\rho)\) represent the diffraction pattern at the back-focal plane and the final image, respectively.

Similarly, for imaging with both elastically and inelastically scattered waves, the process resulting in the intensity on the detector can be described as

\[
\hat{\Gamma}_c(q, q', \Delta E) = \int \Gamma_c(\rho, \rho', \Delta E) e^{-i\rho q} e^{i\rho' q'} d^2\rho d^2\rho', \tag{3.4}
\]

\[
\hat{\Gamma}_i(q, q') = \int \hat{\Gamma}_c(q, q', \Delta E) e^{-i\chi(q, \Delta E)} e^{i\chi(q', \Delta E)} A(q) A(q') E_{is}(q, q') E_{fs}(q, q') p(\Delta E) d\Delta E \tag{3.5}
\]

\[
\Gamma(\rho, \rho') = \int \hat{\Gamma}_i(q, q') e^{i\rho q} e^{-i\rho' q'} d^2q d^2q', \tag{3.6}
\]

\[
I(q) = \int \Gamma(\rho = \rho') e^{-i\rho q} d^2\rho \tag{3.7}
\]

\[
I(\rho) = \int I(q) MTF(q) e^{i\rho d^2q}. \tag{3.8}
\]

Here \(\Gamma_c(\rho, \rho', \Delta E)\) is the exit MCF (Sec. 2.2.2), \(\hat{\Gamma}_i(q = q')\) is the diffraction pattern obtained at the back-focal plane. \(I(\rho)\) represents the final image.

As a summary, the imaging processes for pure elastically scattered wave as well as mixed elastically and inelastically scattered waves are shown in Fig. 3.1

### 3.1 Aberration transfer function

The aberration transfer function of the lens system has the form

\[
e^{-i\chi(q, \Delta E)} = e^{-i[\chi_c(q, \Delta E) + \chi_g(q)]}, \tag{3.9}
\]
3.1. ABERRATION TRANSFER FUNCTION

Figure 3.1: HRTEM imaging process for pure elastically scattered wave as well as mixed elastically and inelastically scattered waves. The equations corresponding to the specific process are marked in blue.

which consists of chromatic aberration $\chi_c(\mathbf{q}, \Delta E)$ and geometric aberration $\chi_g(\mathbf{q})$. The chromatic aberration $\chi_c(\mathbf{q}, \Delta E)$ originates from different focal lengths of the electron beams slightly different in energy. In a rotation-symmetric lens system $\chi_c(\mathbf{q}, \Delta E)$ is expressed as [50]

$$\chi_c(\mathbf{q}, \Delta E) = \frac{\pi C_c \lambda q^2 \Delta E}{E_0}. \quad (3.10)$$

with $\lambda$-the wave length; $C_c$-the chromatic aberration coefficient; $E_0$-accelerating voltage; $\Delta E$-energy loss.

Figure 3.2: Chromatic aberration is caused by different focal length of the electron beams with slightly different energies.

The chromatic aberration is determined by measuring the defocus caused by a small variation of the energy of the incident electron wave. The aberration coefficient $C_c$ can be calculated by linear fitting [14],

$$\Delta f(E_0 + \Delta E) = C_c \frac{\Delta E}{E_0}. \quad (3.11)$$

The chromatic spread is defined as [14]

$$\sigma(f) = C_c \frac{\sigma(E)}{E_0}, \quad (3.12)$$

where $\sigma(E)$ is the standard deviation of the beam energy. On a $C_s$-corrected and $C_c$-uncorrected low-voltage microscope, chromatic aberration is the main factor deter-
mining the information limit of the microscope, which is defined as \[ \frac{\pi \sigma(f) \lambda}{2}. \]

Here \( \sigma(f) \) is the focal spread. For a \( C_s \)-corrected and \( C_c \)-uncorrected microscope \( \sigma(f)=5 \) nm. As can be seen, the effect of the chromatic aberration is strongly increased for large wave lengths.

Geometric aberration \( \chi_g \) can be expanded into a polynomial series \[83\]:

\[
\frac{\chi_g(q, \phi)}{2\pi} = \frac{1}{2} A_1 \lambda q^2 \cos(2(\phi - \phi_{A_1})) + \frac{1}{2} \lambda C_1 q^2 \quad (\text{2-fold astigmatism})
\]

\[
+ \frac{1}{3} A_2 \lambda^2 q^3 \cos(3(\phi - \phi_{A_2})) + \frac{1}{3} \lambda C_2 q^3 \quad (\text{3-fold astigmatism})
\]

\[
+ B_2 \lambda^2 q^3 \cos(\phi - \phi_{B_2}) \quad (2^{nd}\text{-order coma})
\]

\[
+ \frac{1}{4} A_3 \lambda^3 q^4 \cos(4(\phi - \phi_{A_3})) + \frac{1}{4} \lambda C_3 q^4 \quad (3^{rd}\text{-order spherical aberration})
\]

\[
+ \frac{1}{4} A_4 \lambda^3 q^4 \cos(2(\phi - \phi_{A_4})) + \frac{1}{4} \lambda C_4 q^4 \quad (2^{nd}\text{-order star aberration})
\]

\[
+ \frac{1}{5} A_5 \lambda^5 q^6 \cos(5(\phi - \phi_{A_5})) + \frac{1}{5} \lambda C_5 q^6 \quad (5^{th}\text{-order spherical aberration})
\]

\[
+ B_4 \lambda^4 q^6 \cos(4(\phi - \phi_{B_4})) + D_4 \lambda^4 q^6 \cos(3(\phi - \phi_{D_4})) + D_4 \lambda^4 q^6 \cos(3(\phi - \phi_{D_4})) \quad (3-lobe aberration)
\]

\[
+ \frac{1}{6} A_3 \lambda^5 q^6 \cos(6(\phi - \phi_{A_5})) + \frac{1}{6} \lambda C_3 q^6 \quad (6^{th}\text{-order astigmatism})
\]

\[
+ \frac{1}{6} A_4 \lambda^5 q^6 \cos(2(\phi - \phi_{A_4})) + \frac{1}{6} \lambda C_4 q^6 \quad (5^{th}\text{-order astigmatism})
\]

\[
+ B_5 \lambda^5 q^6 \cos(5(\phi - \phi_{B_5})) + D_5 \lambda^5 q^6 \cos(4(\phi - \phi_{D_5})) + D_5 \lambda^5 q^6 \cos(4(\phi - \phi_{D_5})) \quad (4-lobe aberration)
\]

\[+ \ldots \]

Fig. 3.3 shows the imaginary part of the geometric phase transfer function \( \sin \chi_g \) including different aberrations. Here the rotation angle \( \phi_A \) of each aberration is set to 0.

The measurement of the geometrical lens aberrations is usually performed by means of the Zemlin-tableau method \[84\]. This method records the diffractograms of an amorphous specimen using a sequence of tilted beams. The diffractogram obtained by a perfect round lens contains a series of concentric rings. The tilting introduces rotationally symmetric phase shifts such as defocus as well as non-rotationally symmetric phase shifts such as coma and astigmatisms. The coefficients of the introduced aberration coefficients are written as functions of other aberration coefficients. By measuring the contrast transfer functions at different tilting angles, one can determine the induced 2-fold astigmatism coefficient and defocus, thus can retrieve other aberration coefficients from a group of overdetermined linear equations by least-square fitting \[83\].

The residual aberrations are eliminated by multiple elements placed at defined positions within the corrector. In principle, a system which produces adjustable aberrations can also be utilized for correcting them. The symmetry as well as the order of aberration it produces depends on the number of magnetic poles of the lens \[85\] - an electromagnetic
Figure 3.3: Imaginary part of the geometrical aberration transfer function for different aberrations. Here the rotation angle $\phi_x$ of each aberration is set to 0. The corresponding aberration coefficients are marked under each image, and the meaning can be found in Eq. (3.14).
lens with $2m$ magnetic poles introduces the aberration with the $m$–fold symmetry of the order $m - 1$ or higher. For example, quadrupoles introduce 2–fold aberrations with the order of 1, which is eliminated by a quadrupole stigmator producing a 2–fold astigmatism. Hexapoles introduce 3–fold aberrations with the order of $2m$ and a rotationally symmetric third-order combination aberration.

The standard hexapole corrector consists of a telescopic round lens doublet and two hexapoles, one placed at the front focal plane of the first round lens and the other at the back-focal plane of the second round lens (Fig. 3.4). Due to the arrangement of the lenses, the threefold astigmatism of the entire system cancels out, whereas the adjustable negative spherical aberrations of the hexapole elements add up, thus enabling correction of the positive spherical aberration of the objective lens. [86]. Usually the alignment with the help of Zemlin-tableau method has to be carried out several times until all diffractograms recorded at different tilting angles are symmetrically distributed around the center diffractogram. On a $C_s$–corrected microscope, a perfect alignment should result in circular patterns in all the diffractograms (Fig. 3.5). In this case, one
only has to adjust the defocus $\Delta f$ and the 3rd-order spherical aberration to obtain a contrast-optimized image [87]. The geometrical aberrations $\chi_g(q)$ in Eq. (3.14) reduce to

$$
\chi_g(q) = \pi (\lambda \Delta f q^2 + \frac{1}{2} C_s \lambda^3 q^4 + \frac{1}{3} C_5 \lambda^5 q^6).
$$

(3.15)

Here the 5th-order spherical aberration coefficient $C_5$ is a fixed value, which is 4 nm for the latest $C_s/C_c$-corrector. For a $C_s$-corrected microscope, the information limit is mainly determined by the chromatic aberration, and the influence of $C_5$ below the information limit can be neglected. For example, the information limit of the SALVE I microscope ($C_s$-corrected) at 20 kV is 0.23 Å$^{-1}$. However, the contribution of $C_5$ to $\sin \chi_g$ is nearly 0 for $q < 0.3$ Å$^{-1}$.

Information limit can be evaluated according to the size of the usable phase plate (usable aperture). Compared with the information limit defined by Eq. (3.13) in the case of $C_s$-corrected but $C_c$-uncorrected microscope, $d_i$ can be defined more generally as

$$
d_i = \frac{\lambda}{UA}.
$$

(3.16)

Here $UA$ is the size of the usable aperture, determined by all the resolution limiting factors. For the $C_s$-corrected SALVE I microscope the maximum usable aperture is around 20 mrad. On the current $C_s/C_c$-corrected SALVE II microscope, the maximum usable aperture is around 50 mrad, which effectively improves the information limit or the instrumental resolution $d_i$. Fig. 3.6 shows the theoretical resolution improvement obtained by using the usable aperture of 50 mrad - 1.7 Å at 20 kV, 1.2 Å at 40 kV, 1 Å at 60 kV and 0.8 Å at 80 kV.

Figure 3.6: The theoretical instrumental resolution $d_i$ as a function of the accelerating voltage for the usable aperture of 20 mrad and 50 mrad.

### 3.2 Image spread and focus spread

*Image spread* is caused by all kinds of noise inducing a random deflection of the image. The origin of these 0th-order aberrations are vibrations and drift of the stage, parasitic
time-dependent fields resulting from instabilities of the lens currents and from magnetic fields caused by eddy currents in the material of the lenses as shown recently by Uhlemann et al.\[33\]. The combined effect of these disturbances on the image contrast is given by the envelope function \[14\]

\[
E_{\text{is}}(q,q') = \exp\left\{ - \frac{(2\pi)^2}{2} \left[ \sigma^2(x)(q_x - q_x')^2 + \sigma^2(y)(q_y - q_y')^2 \\
+ 2\sigma^2(x,y)(q_x - q_x')(q_y - q_y') \right] \right\}.
\]

(3.17)

Here \(\sigma(x)\) and \(\sigma(y)\) are the rms image spread in the \(xz\)- and \(yz\)- parts. The coefficient \(R = \sigma^2(x,y)/[\sigma(x)\sigma(y)]\) describes the correlation between the image spread in the two parts. In the isotropic case, there is no correlation between the image spread in the two perpendicular directions and we have \(\sigma(x) = \sigma(y) = \sigma_z\) and \(\sigma(x,y) = 0\). Then Eq. (3.17) reduces to

\[
E_{\text{is}}(q,q') = \exp\left\{ - \frac{(2\pi\sigma_z)^2}{2} (q^2 + q'^2 - 2qq') \right\} = \exp\left\{ - \frac{(2\pi\sigma_z)^2}{2} (q - q')^2 \right\}.
\]

(3.18)

The residual focus spread is caused by all the stage- and lens instabilities causing movements in the \(z\)-direction and by the parasitic first-order aberrations of the focusing elements. Here we use the term ‘residual’ to indicate that the focus change has nothing to do with the chromatic aberration, but in essence, the residual focus spread has the same influence as the chromatic aberration. The effect of the focus spread on the image contrast is expressed by the envelope function \[14\]

\[
E_{\text{fs}}(q,q') = \exp\left\{ - \frac{(\pi\lambda)^2}{2} \left[ \sigma^2(f_x)(q_x^2 - q_x'^2)^2 + \sigma^2(f_y)(q_y^2 - q_y'^2)^2 \\
+ 2\sigma^2(f_x,f_y)(q_x^2 - q_x')(q_y^2 - q_y')(q_x'^2 - q_y'^2) \right] \right\},
\]

(3.19)

where \(\sigma(f_x)\) and \(\sigma(f_y)\) account for the rms focus spread in \(xz\)- and \(yz\)- sections, and \(R = \sigma^2(f_x,f_y)/[\sigma(f_x)\sigma(f_y)]\) indicates the correlation of the focus spread in the two sections. For round lenses, the focus spread is isotropic and \(\sigma(f_x) = \sigma(f_y) = \sigma(f)\). Then Eq. (3.19) reduces to the form:

\[
E_{\text{fs}}(q,q') = \exp\left\{ - \frac{(\pi\lambda\sigma_f)^2}{2} (q^2 + q'^2 - 2qq'^2) \right\} = \exp\left\{ - \frac{(\pi\lambda\sigma_f)^2}{2} (q - q')^2 \right\}.
\]

(3.20)

### 3.3 Transfer feature of the camera

Each pixel on the CCD camera is a sensor made of p-type semiconductor. The imaging electrons are first converted into photons in the scintillator made of YAG (yttrium aluminum garnet) or phosphor, and the photons generate electrons which occupy the potential wells in the depleted layer of the p-type semiconductor. The number of electrons in the potential wells is proportional to the photon intensity, and these electrons are then collected and shifted to the read-out device \[81\].

The average number of electrons \(N_j\) detected by the \(j\)th detector pixel is determined by the electron dose \(D\), the magnification ratio \(M\) which together with the physical size
of the pixel $\delta p$ determines the sampling $\delta = \delta p / M$, and the probability of the electron hitting the pixel $I_j$, namely

$$N_j = D\delta^2 I_j = DI_j\left(\frac{\delta p}{M}\right)^2.$$  

The actual number of electrons collected by each detector pixel is governed by Poisson distribution, indicating that the number of electrons collected by the $j$th detector pixel lies mostly within the range $[N_j - \sqrt{N_j}, N_j + \sqrt{N_j}]$.

The SNR of the whole image is evaluated as

$$\text{SNR} = \frac{\bar{N}}{\sigma(N)},$$

where $\sigma(N)$ is the standard deviation of the electron number collected by each pixel and the average number of electrons per image pixel $\bar{N}$ is defined as

$$\bar{N} = \frac{1}{J} \sum_{j=1}^{J} N_j = \frac{D\delta^2}{J} \sum_{j=1}^{J} I_j = D\delta^2 \bar{I}.$$  

Here $J$ is the total number of image pixels, and $\bar{I}$ is the average image intensity. We define the actual number of electrons collected by the $j$th image pixel as $\text{Pois}(D\delta^2 I_j)$, then

$$\sigma(N) = \sqrt{\frac{1}{J} \sum_{j=1}^{J} [\text{Pois}(D\delta^2 I_j) - \text{Pois}(D\delta^2 \bar{I})]^2}.$$  

(3.24)

If $I_j = \bar{I}$ for any image pixel, indicating that the probability of the electrons hitting each image pixel is the same, then $\sigma(N) = \sqrt{D\bar{I}\delta} = \sqrt{\bar{N}}$ and $\text{SNR} = \frac{\bar{N}}{\sigma(N)}$.

Since an incident electron can cause photon excitation in an area of 50-100 $\mu m^2$, which is larger than the physical size of the pixel [81], this electron can be detected by several neighboring pixels and this point-spread feature is characterized by the PSF of the detector. Depending on the sampling - the actual dimension each pixel represents, the influence of the point-spread feature on the image is controllable. Generally speaking, the finer the sampling is, the actual dimension represented by the point-spread feature is smaller and sharper. In this case, the MTF of the camera, which is the Fourier transform of the PSF, gets flatter and is close to the constant 1. As a result, the influence of the MTF on the image contrast becomes negligible (Eq. (3.3)).
Part II

Experiment
Chapter 4

Microscopes

The experiments within the frame of the SALVE project are mainly performed on the FEI Titan Microscope and the SALVE microscopes based on Zeiss LIBRA 200 MC TEM. The sketches of the Titan microscope and the SALVE I prototype are shown in Fig. 4.1.

The instability of the high tension produces an energy broadening of the electron beam. In order to obtain a quasi-monochromatic electron beam, the microscope design for SALVE I and II includes a monochromator and a $90^\circ - \Omega$ in-column energy-filter. The monochromator is inserted between the electron gun and the accelerator and consists of four electric prisms to bend the electron beam to $90^\circ$ and two quadrupoles prism to focus the electron beam at the energy-selecting slit [85]. This monochromator can compensate for the second-order geometrical aberrations as well as optimize the third-order aberrations. The difference between the monochromator and the $90^\circ - \Omega$ energy filter is that the energy dispersion plane is inside the monochromator but outside the energy filter (Fig. 4.1 right).

The SALVE II prototype has been optimized to achieve the highest objective lens current stability ($\Delta I/I < 10^{-7}$) within the voltage range between 20 to 80 kV [36]. The monochromator was used with the largest slit of 60 $\mu$m. The size of the energy window of the filter was not limited by an energy-selecting slit but only by the physical limitations such as fixed apertures and tube diameters, resulting in about 130 eV at 40 kV. On the SALVE II prototype, images were acquired using a CMOS (complementary metal oxide semiconductor) based camera of the type TVIPS T416 (4k detector, $16 \times 16 \mu m^2$ pixel size). The fiber-optics coupled scintillator was optimized to obtain large conversion rates and high resolution.

On the FEI Titan 80-300 kV microscope, a post-column energy filter is implemented (Fig. 4.1 left). This energy filter bends the electrons $90^\circ$ with a magnetic prism, and magnifies the spectrum to the energy-selecting slit. Four additional quadrupoles are used to project either the spectrum or the image onto the detector [89]. Images are recorded utilizing a GIF camera (Gatan model US1000). A high post-magnification can be achieved resulting in very fine sampling. In this way, the damping of camera modulation transfer can be minimized (Sec. 3.3).

The microscope parameters applied for image calculations are listed in Tab. 4.1.
Figure 4.1: **Left** - The components on the FEI Titan 80-300 electron microscope. **Right** - the components on the SALVE I prototype based on the Zeiss LIBRA 200 electron microscope. FEI Titan as well as SALVE I is equipped with a hexapole aberration corrector. (The SALVE II microscope, which is not shown here, is equipped with a modified $C_s/C_c$-corrector proposed by Rose and Kuhn [90]. All other components are similar in SALVE I and II.)

Table 4.1: Microscope parameters for different accelerating voltages denoted by HT. UA represents the usable aperture; $C_5$ is the coefficient of the 5th-order spherical aberration; $\sigma(C_5)$ represents the standard deviation of image spread; $\sigma(C_1)$ represents the standard deviation of focus spread; $C_c$ represents the chromatic aberration.

<table>
<thead>
<tr>
<th>Type</th>
<th>HT (kV)</th>
<th>UA (mrad)</th>
<th>$C_5$ (mm)</th>
<th>$\sigma(C_5)$ (pm)</th>
<th>$\sigma(C_1)$ (Å)</th>
<th>$C_c$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titan</td>
<td>80</td>
<td>20</td>
<td>$0^1$</td>
<td>0</td>
<td>$0^2$</td>
<td>1.41</td>
</tr>
<tr>
<td>SALVE I</td>
<td>20</td>
<td>20</td>
<td>$0^1$</td>
<td>31</td>
<td>$0^2$</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>40</td>
<td></td>
<td>4</td>
<td></td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>60</td>
<td>4</td>
<td>40</td>
<td>5</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>80</td>
<td></td>
<td>29</td>
<td>5</td>
<td>1.26</td>
</tr>
</tbody>
</table>

1In the case with only $C_s$ correction, the maximum usable aperture is around 20 mrad, and the corresponding information limits are 4.35 Å at 20 kV and 2.08 Å at 80 kV, respectively. However, the influence of $C_5$ is trivial for the spatial resolution coarser than 3.33 Å at 20 kV and 2 Å at 80 kV, respectively. Therefore $C_5$ can be neglected for Titan and SALVE I microscope.

2Based on Eq. (3.12), we can estimate the chromatic spread. Assuming $\sigma(E)=0.3$ eV for the electron gun, then the chromatic spread is 18.9 nm for the SALVE I microscope at 20 kV and 5.3 nm for the Titan microscope at 80 kV. The magnitude of the residual focus spread for the Titan microscope and SALVE I microscope is only dozens of picometers, which is negligible compared with the chromatic spread.
Chapter 5

Samples

We chose graphene as test object for the image calculations since it is a sample of well defined thickness and moreover, the thinnest possible sample. It can be prepared as a clean, free-standing membrane of precisely mono-atomic thickness \[91\]. Calculations and experiments can thus be compared to each other with much lower uncertainty than for a thicker \(\text{TEM}\) specimen. In addition, graphene has a well-known lattice structure \[92\] and is very stable at electron energies below 80 keV \[93\]. Moreover, graphene is of great practical interest as it exhibits fascinating physical properties \[94\]. The recent development of new preparation methods enables production of large area single-layer and bi-layer graphene of high quality \[95\]-\[98\]. Therefore, basic \(\text{TEM}\) studies of defects in graphene \[92\]-\[98\] or atoms on top of graphene \[101\]-\[102\] can now be performed.

For a correct evaluation of the experimental contrast of graphene images, it is important to calculate the image contrast based on the appropriate model at the voltage necessary for destruction-free imaging. Although, in general, an 80 keV electron beam should suffice for destruction-free \(\text{HRTEM}\) imaging of graphene, deviations from the pristine structure and adsorbate atoms on top of graphene can lead to the removal of carbon atoms even at energies below 80 keV \[35\]-\[103\]-\[104\]. For example, dangling bond atoms at single vacancies can be displaced at energies around 70 keV and edge atoms even at around 50 keV \[105\]. Therefore, imaging at lower voltages is desirable.

Silicon is a common semiconductor widely used in industry for the production of the solar cells and integrated circuits. Here we chose silicon to illustrate the image calculation for the multilayered structure out of the following reasons:

As \(\text{TEM}\) sample, silicon is a paradigm due to its low cost for production and simple structure facilitating the comparison between experiments and calculations. The silicon sample can be as thin as 5 nm thick which provides very good transparency for the electron beam. It is stable under high electron dose and high temperature conditions as well as against plasma cleaning. The dumbbell structure in the \(\langle110\rangle\) projection has a sub-Angstrom distance of 0.78 Å, therefore can be used to test the resolving ability of the microscope.
Figure 5.1: **Left** - The 2D hexagonal structure of graphene with a space group of $P6/mmm$. The C-C bond length is 1.424 Å and the distances 1.23 Å and 2.13 Å correspond to two dominant reflections in the diffraction pattern of graphene. **Right** - The cell structure of silicon with a space group of $Fd\overline{3}m$. The lattice parameter of silicon is 5.431 Å and the Si-Si bond length is 2.35 Å.
Part III

Results
Chapter 6

Image calculation involving elastic scattering

In this chapter we report on image contrast calculations for graphene imaged with 80 keV and 20 keV electrons following the approach used in [48–50], which takes into account the finite energy distribution of the imaging electrons by an explicit summation over many images calculated with slightly different energies.

However, instead of approximating this energy distribution by a Gaussian [48] or Maxwell distribution [50], we normalize the experimentally acquired zero-loss peak extracted from EELS data. This includes the energy distribution of the source and all additional energy broadening effects due to instabilities. Our approach is carried out in three steps:

1. Exit wave calculation. The exit-wave is calculated applying the Wentzel potential (Appendix 3.2) with multislice method (see Sec. 2.1.5). Since we consider a single-atomic layer thick sample, the multislice simulation reduces to a single-slice calculation.

2. Normalization of the zero-loss peak (determination of the weighting factor $p(\Delta E)$ in Eq. (3.2)). After the electrons have transmitted through the object, their energy distribution has been changed due to inelastic scattering, which can be measured from the corresponding EELS data. However, the inelastically scattered electrons are removed by an energy filter and do not contribute to the image contrast. Therefore we only need to consider the area under the zero-loss peak. The normalized zero-loss peak provides a weighting function $p(\Delta E)$ satisfying $\int p(\Delta E)d(\Delta E) = 1$. This function includes all contributions to the energy spread of the primary beam.

3. The image is calculated following Eqs. (3.1)-(3.3).

In our image calculation, we have evaluated the atom contrast after Watson et al. [106]. In order to make the sign consistent with the definition of Zernike [107], where the atom appears darker than the background for positive contrast (dark atom contrast), and brighter for negative contrast (bright atom contrast), we express the atom contrast $C_W$.

\[ C_W = \frac{\rho_{\text{atom}} - \rho_{\text{background}}}{\rho_{\text{atom}} + \rho_{\text{background}}} \]

This chapter is adapted based on [74].
\[ CW = \frac{I_b - I_a}{I_b}. \]

Here \( I_a \) is the image intensity at the center of the atom, and \( I_b \) is the intensity of the background.

Utilizing the calculation procedure introduced above with a series of changing \( C_s \) and \( \Delta f \) (-100 \( \mu \text{m} \leq C_s \leq 100 \mu \text{m} \) with the increment of 0.5 \( \mu \text{m} \), -30 nm \( \leq \Delta f \leq 30 \) nm with the increment of 0.2 nm), we can determine the optimal imaging conditions for obtaining the maximum atom contrast. By comparing the maximum atom contrast for bright atom imaging and dark atom imaging, we can judge the validity of the WPOA at 80 kV and 20 kV. Moreover, we explore the dependence of atom contrast as a function of chromatic aberration and the energy resolution (energy width). Single-layer graphene samples were prepared by mechanical cleaving and transferred to TEM grids as described previously [108]. The EELS spectra was recorded from single-layer graphene regions on FEI Titan 80-300 equipped with a Tridiem GIF spectrometer for 80 kV and on a monochromated Zeiss Libra 200 equipped with an in-column energy filter for 20 kV.

### 6.1 Optimum imaging conditions for graphene with and without chromatic aberration

The calculation was performed for different microscope settings listed in Tab. 6.1. Part of the calculated \((C_s, \Delta f)\) tables for graphene imaged under 80 kV with achromatic imaging conditions are shown in Fig. 6.1. Interestingly, the images look very similar for a wide range of \((C_s, \Delta f)\) values, encircled by the blue contours in Fig. 6.1 a) and b). The two images marked by the red rectangles are selected as representatives for bright and dark atom contrast, respectively.

Fig. 6.2 presents calculated images of graphene at 80 kV. The two chosen marked images from Fig. 6.1 are depicted in the middle column (SALVE II). The images in the left column (Ideal) and in the right column (Titan) are selected from the corresponding \((C_s, \Delta f)\) tables in the same way. The images in Fig. 6.3 are chosen from the corresponding \((C_s, \Delta f)\) tables for 20 kV.

At 80 kV (see Fig. 6.2), the measured energy distribution on the Titan microscope shows a FWHM of 0.35 eV, which results in strong chromatic aberration (Eq. 3.12). In this case the maximum positive and negative contrasts almost cancel each other (right column in Fig. 6.2). In the achromatic imaging condition with the residual image spread and focus spread, the maximum positive and negative atom contrasts are more than twice compared with the values in the third column (middle column in Fig. 6.2). The discrepancy between the maximum positive and negative contrasts increases to about 2%. In the ideal case where there is no damping functions existing, the maximum atom contrasts can reach -26.6% for bright atom and -21.6% for dark atom, respectively. Compared with the third column, the maximum bright atom contrast quadruples in the ideal case! The discrepancy between the maximum positive and negative contrast enlarges to 5%. At 20 kV, the discrepancy can reach as large as 13% (1st column in Fig. 6.3).

At 20 kV (see Fig. 6.3), the measured energy distribution shows a FWHM of 0.12 eV obtained with the monochromator. Without chromatic aberration correction (compare
6.1. OPTIMUM IMAGING CONDITIONS

Figure 6.1: Image calculation for graphene recorded with $C_c/C_s$-corrected SALVE II microscope operated at 80 kV. Part of the calculated $(C_s, \Delta f)$ table showing a) bright atom contrast and b) dark atom contrast. High bright atom contrasts around -15% are obtained for a set of $(C_s, \Delta f)$ values marked by the blue contour in a). Similarly, high dark atom contrasts around 13% are obtained for a set of $(C_s, \Delta f)$ values marked by the blue contour in b). The two images marked by the red rectangles are in the centre of the highest-contrast diagonal representing optimum contrast values (-17.2% for bright atom contrast and 13.5% for dark atom contrast). Scale bar: 0.2 nm
CHAPTER 6. CALCULATION INVOLVING ELASTIC SCATTERING

Table 6.1: Aberration parameters and image spread used for the simulation of images at an accelerating voltage of 20 kV and 80 kV. UA defines the usable aperture; $C_c$ is the chromatic aberration coefficient; $C_s$ and $C_5$ are the coefficients of the 3rd-order and 5th-order spherical aberration, respectively; $\Delta f$ is the defocus; $\sigma(C_1)$ and $\sigma(C_s)$ represent the standard deviation of the residual focus spread and the image spread, respectively.

<table>
<thead>
<tr>
<th>HT (kV)</th>
<th>Type</th>
<th>$C_c$ (mm)</th>
<th>Contrast</th>
<th>$C_s$ (µm)</th>
<th>$\Delta f$ (Å)</th>
<th>$C_5$ (mm)</th>
<th>$\sigma(C_s)$ (pm)</th>
<th>$\sigma(C_1)$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>Ideal</td>
<td>0</td>
<td>bright</td>
<td>-5</td>
<td>70</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>dark</td>
<td>5</td>
<td>-70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SALVE II</td>
<td>0</td>
<td>bright</td>
<td>-13</td>
<td>98</td>
<td>4</td>
<td>47</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>dark</td>
<td>-3</td>
<td>-40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SALVE I</td>
<td>1.26</td>
<td>bright</td>
<td>0</td>
<td>30</td>
<td>0</td>
<td>31</td>
<td>0^2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>dark</td>
<td>2</td>
<td>-40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>Ideal</td>
<td>0</td>
<td>bright</td>
<td>-3</td>
<td>40</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>dark</td>
<td>3</td>
<td>-40</td>
<td></td>
<td></td>
<td></td>
</tr>
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<td></td>
<td>SALVE II</td>
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<td>-11.5</td>
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<td>26</td>
<td>5</td>
</tr>
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<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Titan</td>
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<td>60</td>
<td>0^1</td>
<td>0</td>
<td>0^2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>dark</td>
<td>0</td>
<td>-50</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 Please refer to footnote [1] of Tab. 4.1.
2 Please refer to footnote [2] of Tab. 4.1.

Figure 6.2: 80 kV-TEM images of graphene calculated for optimum contrast conditions showing negative (upper row) and positive (lower row) carbon atom contrast, respectively. The corresponding maximum contrast values (multiplied by 100) are given in the right lower corner of each image, and the aberration parameters are given in Tab. 6.1. From left to right: Ideal case ($C_c = 0, C_5 = 0$), SALVE II microscope ($C_c = 0$, $C_5 = 4$ mm) and Titan microscope ($C_c = 1.41$ mm, $C_5 = 4$ mm) with the energy distribution acquired from normalized experimental zero loss peak. The inset here depicts the experimental zero-loss peak with an energy width of $E_w = 0.35$ eV used for the calculations.
the 3rd columns in Fig. 6.3 and Fig. 6.2, the absolute values of optimum positive and optimum negative contrast at 20 kV is much lower than at 80 kV. Under the achromatic imaging condition ($C_c = 0$) with the residual focus spread and image spread (given in Tab. 6.1), the atom contrast in the 20 kV case is still 2% lower than that in the 80 kV case (compare the 2nd columns in Fig. 6.3 and Fig. 6.2). A remarkable increase of the atom contrast is only shown when all damping functions are eliminated (compare the left columns in Fig. 6.2 and Fig. 6.3). As a short summary, chromatic aberration not only weakens the atom contrast, but also reduces the difference between the maximum positive and negative atom contrasts. Other damping functions like image spread and focus spread have similar effects, however not as strong as chromatic aberration.

![Figure 6.3: HRTEM images of graphene at 20 kV for optimum contrast conditions showing negative (upper row) and positive (lower row) carbon atom contrast, respectively. The corresponding maximum contrast (multiplied by 100) are given in the images, and the aberration parameters are given in Tab. 6.1. From left to right: Ideal case ($C_c = 0, C_5 = 0$), SALVE II microscope ($C_c = 0, C_5 = 4$ mm) and SALVE I microscope ($C_c = 1.26$ mm, $C_5 = 0$ mm) with the energy distribution acquired from normalized experimental zero loss peak. The inset here depicts the experimental zero-loss peak with an energy width of $E_w = 0.12$ eV used for the calculations.]

The achromatic bright atom contrast image in Fig. 6.3 (20 kV) demonstrates two very strong contrast enhancement effects by comparing the images in the first column. The effect of bright atom contrast enhancement has already been mentioned in [109,110]. At 20 kV, even for a highly monochromatic electron source, resulting in a small $E_w$ of 0.12 eV, the atom contrasts are almost nullified for both bright and dark imaging. Hence the correction of chromatic aberration and bright atom contrast imaging conditions are indispensable for achieving high contrast at voltages as low as 20 kV.

6.2 Validity of the WPOA at low voltages

The achromatic image calculations show symmetric ($C_s, \Delta f$) values for optimum negative and positive atom contrast for both, 80 kV and 20 kV (see Tab. 6.1, the left columns in Fig. 6.3 and Fig. 6.2). However, the respective absolute contrast values differ considerably. This is a fingerprint of the contributions from non-linear terms to the image contrast. The absolute contrast difference increases as the voltage decreases.
In Appendix C we have shown that in order to treat an object as an ideal weak phase object, the absolute values of optimum positive and optimum negative contrast must be roughly equal for achromatic imaging conditions (other damping effects should also be negligible). When the voltage drops from 80 kV to 20 kV, the contribution of non-linear terms to the image contrast can no longer be ignored since the interaction parameter $\sigma$ increases with decreasing voltage.

Furthermore, we can prove the failure of the WPOA at 20 kV by investigating the scattering amplitude, which is a complex (Sec. 2.1.2). The integral of the modulus of the scattering amplitude over the scattering solid angle results in the scattering cross section (Sec. 2.1.1).

Fig. 6.4 shows the scattering cross-sections calculated for single atoms at 20 kV and 80 kV, respectively. The scattering cross-sections based on the WPOA are calculated according to Eq. (B.14), and the scattering cross-sections based on the POA are calculated according to Eq. (B.15). At 80 kV, the scattering cross-sections based on both approximations are very close, however at 20 kV, the values are only equal for atoms with atomic number larger than 16. By examining the phase of the scattering amplitude $\eta(\theta)$, one can see the discrepancy between the two approximations more clearly. The phase of the scattering amplitude can be calculated based on Eq. (B.16). For the WPOA the scattering amplitude is the Fourier transform of the potential energy of the incident electron (Sec. 2.1.3). Since the potential energy is real, the scattering amplitude based on the WPOA is also real, which indicates that the corresponding phase is 0, as shown by the black dot line in Fig. 6.5 for a single carbon atom. Based on the POA the phase of the scattering amplitude is never 0 even for a light atom like carbon. At 20 kV, the phase discrepancy between the WPOA and the POA is large, more remarkable than at 80 kV, which indicates once again that the WPOA fails at 20 kV. Even light atoms such as carbon are strong electron scatterers under this accelerating voltage. Moreover, there may be significant contributions due to inelastic scattering at 20 kV, which are not yet considered. As we neglect inelastic scattering in our current
6.3 Contrast dependence on chromatic aberration and energy width

In the following we investigate the dependence of the optimum atom contrast on chromatic aberration (Fig. 6.6a) and energy width (Fig. 6.6b) in more detail. In order to show the influence of both chromatic aberration and the energy broadening of the imaging electrons exclusively, we have neglected all the other damping functions like focus spread and image spread. Fig. 6.6 shows that the absolute optimum atom contrast at 20 kV decreases strongly with increasing $C_c$ (Fig. 6.6a, red curves) and $E_w$ (Fig. 6.6b, red curves), respectively; much stronger than at 80 kV (Fig. 6.6a and b, blue curves). At 20 kV, the values of bright and dark atom contrasts (light and dark colors, respectively) are large for the achromatic case ($C_c = 0$, $E_w = 0$). Without chromatic aberration and other damping functions, the constructive superposition of linear and non-linear terms results in enhanced contrast (bright atom contrast) [109]; while the destructive superposition results in reduced contrast (dark atom contrast). With increasing chromatic aberration, bright atom contrast decreases faster than dark atom contrast. As a result, both curves intersect each other, as shown in Fig. 6.6a. At 20 kV, a contrast improvement of about a factor of 2 (from about 8% to 16%) can be achieved with a monochromator, which reduces the energy width from $E_w \sim 0.35 \text{ eV}$ to 0.12 eV (as marked by the corresponding dashed lines in Fig. 6.6). However, this behavior does not hold true in the case of 20 kV. Fig. 6.6b shows that for 20 kV, the contrast drops to about zero in presence of chromatic aberration for energy widths larger than about 0.2 eV. For the achromatic case, the absolute values of bright and dark atom contrast and their differences are much larger at 20 kV than at 80 kV. At 20 kV, even the use of an effective monochromator (0.12 eV energy width) is not sufficient because the resulting optimum contrast values are close to zero. However, the addition of $C_c$ correction
Figure 6.6: (a) Calculated absolute optimum atom contrast of graphene as a function of the chromatic aberration coefficient $C_c$ and (b) as a function of the energy width ($E_w$) of the zero loss peak for 20 kV (red circle) and 80 kV (blue triangle) for bright (light colour) and dark (strong colour) atom contrast. The corresponding experimental parameters for $C_c$ and $E_w$ are taken from the Titan microscope and SALVE I microscope, indicated by the dashed lines. The variable energy width in b) is obtained by proportionally shrinking or stretching the zero-loss peak extracted from the experimental EELS data. The energy width used for the calculation in a) is $E_w=0.12$ eV for 20 kV and $E_w=0.35$ eV for 80 kV. The chromatic aberration used for the calculation in b) is $C_c=1.21$ mm for 20 kV and $C_c=1.41$ mm for 80 kV. Reproduced from Ultramicroscopy with the reference [74].
tremendously increases the contrast in 20 kV TEM images. Hence, $C_c$ – corrector is one of the keys for obtaining high image contrast at low voltages.

6.4 Contrast dependence on image spread and focus spread

In this short section we investigate the dependence of the optimum bright atom contrast on image spread (Fig. 6.7a) and focus spread (Fig. 6.7b). All the bright atom contrasts are calculated under achromatic imaging condition. Fig. 6.7a shows that the absolute optimum bright atom contrast at 20 kV decreases with increasing $\sigma(C_\epsilon)$, more remarkably than at 80 kV. At 80 kV, a contrast increase of about a factor of 2 (from about 14% to 28%) can be achieved by the elimination of image spread. (The current value of $\sigma(C_\epsilon)$ on the $C_s/C_c$-corrected SALVE II microscope is 26 pm at 80 kV, marked by the corresponding dashed blue line in Fig. 6.7a.) At 20 kV, the contrast can be increased with a factor of 3 by eliminating the image spread. (The current $\sigma(C_\epsilon)$ on the $C_s/C_c$-corrected SALVE II microscope is 47 pm at 20 kV, marked by the corresponding dashed red line in Fig. 6.7a.) Fig. 6.7b shows that the damping of focus spread on the image contrast is weak for the current experimental settings, marked by the dashed line in Fig. 6.7b. Hence, on a $C_s/C_c$-corrected microscope, image spread becomes the dominant factor determining the image contrast.

6.5 Conclusions

For 80 kV and 20 kV we have calculated the optimum $C_s$ -corrected HRTEM image contrast exemplified by graphene. We calculated, for the first time, the image intensity by averaging over the energy distribution of the elastically scattered imaging electrons, derived from the experimental EELS data. Significant improvement of contrast can only be achieved by the additional correction of chromatic aberration as well as the elimination of other damping effects like image spread. Moreover, we show that a further increase of contrast is possible by using bright atom imaging conditions, even for a single layer of atoms. Our calculations clearly show that even graphene cannot be treated as a weak phase object at 20 kV. In other words, all atoms are strong scatters at 20 kV.
Figure 6.7: (a) Calculated optimum bright atom contrast of graphene as a function of the standard deviation of the image spread $\sigma(C_\epsilon)$ and (b) as a function of the standard deviation of the focus spread $\sigma(C_1)$ for 20 kV (red circle) and 80 kV (blue circle). The corresponding experimental parameters for $\sigma(C_\epsilon)$ and $\sigma(C_1)$ are taken from the $C_s/C_c$-corrected SALVE II microscope, indicated by the dashed lines.
Chapter 7

Image calculation involving inelastic scattering

As stated in Sec. 2.2.5, the first and most crucial step for the image calculation involving inelastic scattering is to calculate the MDFF. In our model (Eq. (2.145)) based on the Raman-Compton approximation (Eq. (2.114)) and the Wentzel model (Appendix B), the difficulty for the image calculation lies in the first term in Eq. (2.145), which results in a 4D Fourier transform during the calculation procedure. For our multislice algorithm, the 4D Fourier transform over each sample slice is computationally time-consuming, and therefore the factorization of the MDFF into combinations of independent functions with respect to $\theta$ and $\theta'$ is desired. With this aim in mind, we have developed a new approximation for the MDFF (Appendix D) and applied this approximation for the image calculation.

We have calculated zero-loss filtered images and plasmon-loss filtered images for graphene and Si(110) for the $C_s/C_c$-corrected SALVE II microscope operated at 20 kV. A zero-loss filtered image is contributed by the elastically scattered electrons, corresponding to Case A in Fig. 2.5. A plasmon-loss filtered image is contributed by the inelastically scattered electrons causing plasmon excitations, corresponding to Case B in Fig. 2.5. Graphene and Si(110) are chosen to illustrate the influence of inelastic scattering on a one-atom thin sample (graphene) and on a thin classical 3D sample (silicon), respectively.

We calculated the outgoing MCFs following the procedure introduced in Sec. 2.2.5 as well as the final images following Eqs. (3.4)-(3.8). The energy distribution $p(\Delta E)$ in Eq. (3.5) is obtained from the experimental EELS spectra. In the case of zero-loss filtered images, the energy distribution $p(\Delta E)$ corresponds to the zero-loss peak of the EELS spectra. In the case of plasmon-loss filtered images, $p(\Delta E)$ corresponds to the plasmon-loss region of the EELS spectra. The energy distribution over both the zero-loss peak and the plasmon-loss region is normalized:

$$\int_{ZL+PL} p(\Delta E)d(\Delta E) = 1.$$  \hspace{1cm} (7.1)

The corresponding aberration parameters providing the maximum atom contrast are determined by the procedure described in Chap. 6. The parameters for the calculations

1This chapter is adapted based on [75].
Table 7.1: Parameters utilized by the image calculation for graphene and Si⟨110⟩ on the SALVE II microscope operated at 20 kV. $C_s$ is the coefficient of the third-order spherical aberration; $\Delta f$ is the defocus; $\sigma (C_1)$ and $\sigma (C_5)$ represent the standard deviation of the focus spread and the image spread, respectively.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Graphene</th>
<th>Si⟨110⟩</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample thickness (Å)</td>
<td>3.35</td>
<td>167±10</td>
</tr>
<tr>
<td>No. of atomic layers</td>
<td>1</td>
<td>88</td>
</tr>
<tr>
<td>sampling (Å/pixel)</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>$C_\epsilon$ (mm)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$C_s$ (µm)</td>
<td>-13</td>
<td>-6</td>
</tr>
<tr>
<td>$\Delta f$ (Å)</td>
<td>98</td>
<td>38</td>
</tr>
<tr>
<td>$C_5$ (mm)</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>$\sigma (C_1)$ (Å)</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>$\sigma (C_5)$ (pm)</td>
<td>47</td>
<td>47</td>
</tr>
</tbody>
</table>

The sample thickness of Si⟨110⟩ is determined by the experimental EELS spectra with log-ratio method [111] to 16.7±1 nm. For graphene the thickness of one single layer is assumed to be 0.335 nm, which is the layer thickness of graphite. For both samples the thickness is sufficiently small that multiple inelastic scattering can be neglected, which is proved by the experimental EELS spectra where only one plasmon peak exists.

Experimental energy-loss spectra of both Si⟨110⟩ and free-standing single-layer graphene were recorded using the SALVE II prototype microscope (Sec. 4). The energy resolution is 0.16 eV for graphene and 0.23 eV for silicon, respectively. The energy-loss spectra were recorded in image-mode with a collection semi-angle of 7.7 mrad for Si⟨110⟩ and 10 mrad for graphene determined by the objective aperture. The entrance aperture of the energy filter limited the illuminated sample area to less than 200 nm in diameter.

The semi collection angle for the EELS spectra is large enough for collecting all the low-loss scattered electrons. For example in the case of silicon⟨110⟩, the first plasmon-loss peak extends to the energy loss of 25 eV, and the characteristic inelastic scattering angle at 20 kV is

$$\theta_E = \frac{\Delta E}{2E_0} = \frac{25}{2 \times 20000} = 0.6 \text{ mrad} \ll 7.7 \text{ mrad}. \quad (7.2)$$

For thin samples, this angle is also large enough for collecting most of the zero-loss electrons because the zero-loss electrons are mainly included in the center (forward-scattered) beam, which can be shown by comparing the intensity of the diffraction spots in the center and at other reflections. The ratio between the intensity of center spot and other reflections increases in a negligible way when the collection angle increases. However, for thick samples the increase of the collection angle indeed results in a difference due to larger and larger scattering angles caused by multiple scattering. In the case of silicon with a thickness of 16.7 nm, we estimate that the influence of the collection angle is negligible.

### 7.1 Image calculation for graphene at 20 kV

The absorption factor $\mu_2$ was calculated based on Eq. (2.135) and Eq. (2.147), with the MDFF $S(K, K', \Delta E)$ derived utilizing the Raman-Compton approximation (Eq.
7.1. IMAGE CALCULATION FOR GRAPHENE AT 20 KV

and the Wentzel model (Eq. 2.145). The influence of the absorption factor $\mu_2$

Figure 7.1: The absorption factor $\mu_2$ calculated for the monolayer graphene at 20 kV. As can be seen, the factor $\mu_2$ for graphene at 20 kV is close to a constant. Reproduced from Ultramicroscopy with the reference [75].

can be seen from Eq. (2.139) - the intensity of the zero-loss filtered image is attenuated by the factor of $\exp(-\mu_2)$. As one can see from Fig. 7.1, the absorption factor $\mu_2$ for graphene at 20 kV is close to a constant (check the color-bar values). Therefore we obtain $\exp(-\langle \mu_2 \rangle) = \exp(-0.0298) \approx 0.74$, and can predict that the intensity of the zero-loss filtered image decreases to 74% compared with the calculation considering pure elastic scattering.

Another reason for the different intensity in Fig. 7.2(b) (pure elastic scattering) and Fig. 7.2(d) (elastic and inelastic scattering) is the factor $b_0$ in Eq. (2.139). In the case of graphene at 20 kV, the coefficients $b_0$ and $b_1$ are fitted based on the value of $\langle \mu_2 \rangle$ which lies within the range [0, 0.5]. The linear fitting of $\exp(x)$ results in $b_0 = 0.97$ and $b_1 = 1.29$, respectively; while for pure elastic scattering we have always $b_0 = 1$, $b_1 = 0$ and $\mu_2 = 0$.

For graphene at 20 kV, the factor $b_0$ reduces the image intensity about 3%. According to the integral of the EELS spectra in Fig. 7.2(b) and (d), only 0.65% of the electrons are inelastically scattered. The dramatic decrease in image intensity in Fig. 7.2(d) compared with the b) is mainly due to the influence of the factor $\mu_2$, indicating the strong interference of the 0.65% inelastically scattered electron waves! This result astonishingly shows that at 20 kV, the elastic image intensity is not dominated by the amount of inelastically scattered electrons, but depends on the interference between the inelastically scattered waves.

The $C_c$-corrected plasmon-filtered image (Fig. 7.2(f)) conserves the elastic contrast (Tab. 7.2), however the image intensity is only 39% of the zero-loss filtered case (Tab. 7.2). The line profiles (Fig. 7.2(g)) show that the total intensity is conserved - the image intensity calculated based on pure elastic scattering (red line) is the sum of the image intensity calculated based on elastic scattering but considering absorption (green line) and the intensity of the plasmon-loss filtered image (blue line).

Tab. 7.2 lists the calculated atom contrast $C_W$ (Eq. 6.1) as well as the atom intensity for the calculated images in Fig. 7.2. The minus sign indicates bright atom contrast according to the definition of Eq. 6.1.
Figure 7.2: Calculated graphene images for the $C_s/C_c$-corrected SALVE II microscope at 20 kV (right column) based on the experimental EELS spectra (left column). Atoms in the images are white. a) The normalized zero-loss peak; b) the zero-loss filtered image without absorption; c) the zero-loss peak extracted from the normalized EELS spectra; d) the zero-loss filtered image with absorption; e) the plasmon-loss peak; f) the plasmon-loss filtered image; g) the line profiles marked in the images b), d) and f). The y-axis shows the intensity and the x-axis shows distance in pixels. Sample thickness: 3.35 Å. Aberration parameters: $C_c = 0$, $C_5 = 4$ mm, $C_s = -13$ μm and $\Delta f = 98$ Å. Scale bar: 2 Å.
Table 7.2: Calculated atom contrast and intensity from graphene images for the \(Cs/Cc\)-corrected SALVE II microscope at 20 kV based on Fig. 7.2. UA-usable aperture; \(I_a\)-atom column intensity; \(I_b\)-background intensity; \(I_v\)-mean intensity; \(C_W\)-atom contrast defined by Eq. (6.1).

<table>
<thead>
<tr>
<th>UA</th>
<th>zero-loss</th>
<th>plasmon-loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 mrad</td>
<td>without absorption</td>
<td>with absorption</td>
</tr>
<tr>
<td>(I_a)</td>
<td>1.0353</td>
<td>0.7455</td>
</tr>
<tr>
<td>(I_b)</td>
<td>0.9156</td>
<td>0.6593</td>
</tr>
</tbody>
</table>

7.2 Image calculation for Si(110) at 20 kV

Si(110) has two different patterns repeating along the \(\langle 110 \rangle\) direction. Fig. 7.3 shows the absorption factor \(\mu_2\) calculated for the two patterns. One can estimate that the factor

\[
\mu_2 \approx 0.48 
\]

decreases the zero-loss filtered image intensity to about \(\exp(-\langle \mu_2 \rangle) = \exp(-0.468) \approx 62\%\), compared with the case considering pure elastic scattering. The coefficients \(b_0\) and \(b_1\) in Eq. (2.139) are linearly fitted based on the value of \(\langle \mu_2 \rangle\) which lies within the range \([0, 0.5]\), and results in \(b_0 = 0.97\) and \(b_1 = 1.29\), respectively. One can predict that the calculated intensity of the zero-loss filtered image is \(\exp(-\langle \mu_2 \rangle) \cdot b_0 = 62\% \times 0.97 \approx 60\%\) of the intensity calculated based on pure elastic scattering, also shown by the Tab. 7.3.

Intensity conservation can be verified, shown by the line profiles in Tab. 7.3 and Fig. 7.4, where the superposition of the green line and blue line results in the red line. Hence the summed intensity of the plasmon-loss filtered image and the zero-loss filtered image considering absorption roughly equals the image intensity calculated based on pure elastic scattering for a \(Cs/Cc\)-corrected microscope.

7.3 The validity of the isolated atom model in the plasmon-loss range

The model for the MDFF in Eq. (2.145) is derived based on an isolated-atom model and therefore does not directly include collective electronic excitations (plasmons). Nevertheless, it is able to mimic the properties of the MDFF also for plasmon excitations in crystals as shown in the following:
Figure 7.4: Calculated Si(110) images for the $C_s/C_c$-corrected SALVE II microscope operated at 20 kV (right column), based on the experimental EELS spectra (left column). Atom columns in the images are white. a) The normalized zero-loss peak; b) the zero-loss filtered image without absorption; c) the zero-loss peak extracted from the normalized EELS spectra; d) the zero-loss filtered image with absorption; e) the plasmon-loss peak; f) the plasmon-loss filtered image; g) the line profiles marked in the images b), d) and f). The y-axis shows the intensity and the x-axis shows distance in pixels. Sample thickness: $16.7 \pm 1 \text{ nm}$. Aberration parameters: $C_c = 0$, $C_5 = 4 \text{ mm}$, $C_s = -6 \mu \text{ m}$ and $\Delta f = 38 \text{ A}$. Scale bar: $2 \text{ Å}$. 
7.4. CONCLUSIONS

Table 7.3: Calculated atom contrast and intensity from Si⟨110⟩ images for the C₈/C₇-corrected SALVE II microscope at 20 kV. UA-usable aperture, Iₐ-atom column intensity, Iᵦ-background intensity, C₇-atom contrast defined by Eq. (6.1).

<table>
<thead>
<tr>
<th>UA: 50 mrad</th>
<th>zero-loss</th>
<th>plasmon-loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iₐ</td>
<td>0.9264</td>
<td>0.5565</td>
</tr>
<tr>
<td>Iᵦ</td>
<td>0.4937</td>
<td>0.2963</td>
</tr>
<tr>
<td>C₇ (%)</td>
<td>-87.7</td>
<td>-87.8</td>
</tr>
</tbody>
</table>

1. By incorporating the experimental energy loss distribution \( p(\Delta E) \), we consider the contribution of plasmon excitation with sufficient accuracy, because the delocalization corresponding to plasmon energy losses is large compared with the mean distance between the neighbour atoms.

2. The angular distribution of inelastic scattering for a given energy loss \( \Delta E \) is calculated in the independent-atom approximation using the Wentzel model. For the diagonal elements \( \mathbf{K} = \mathbf{K}' \), the angular distribution is independent of the atom position \( \rho \), and it can be shown that the scattering profile \( S(\mathbf{K} = \mathbf{K}', \Delta E)/K^4 \) is basically a Lorentz distribution with a cut-off angle:

- For \( \theta_E < \theta \ll \theta_A \), one obtains \( S(\theta, \Delta E)/K^4 \sim 1/(\theta^2 + \theta_E^2) \), which is a Lorentz distribution of the width \( \theta_E \).
- For \( \theta \gg \theta_A \), we obtain similarly \( S(\theta, \Delta E)/K^4 \sim 1/\theta^4 \). This means that the MDFF decays fast for scattering angles larger than the characteristic elastic scattering angle \( \theta_A \). A jellium model predicts that at the scattering angle larger than a cut-off angle \( \theta_c \), inelastic scattering due to plasmon excitation falls sharply [111]. Concerning the scattering profile, the employed approximation for the MDFF shows the same behavior as expected for a homogeneous electron gas.

3. In order to discuss the off-diagonal elements of \( S(\mathbf{K}, \mathbf{K}')/(K^2K'^2) \), we have plotted its Fourier transform \( \mu_{11}(r, r') \) in real space for \( r = r' \) at a fixed energy loss of 16 eV. For a single silicon atom, \( \mu_{11}(r = r') \) is sharply peaked at the atom, but also shows a long tail (see Fig. 7.5a). The MDFF in Eq. 2.145 is given by a superposition of many independent atoms. As the delocalization at low energies is larger than the atom distance in the crystal, and the resulting \( \mu_{11}(r = r') \) is nearly constant (see Fig. 7.5b). We can infer that the off-diagonal elements in \( S(\mathbf{K}, \mathbf{K}')/(K^2K'^2) \) must be small compared to the diagonal elements, which is in perfect agreement with the model of a homogeneous electron gas.

7.4 Conclusions

The image calculation involving multiple elastic scattering and one inelastic scattering event is mainly associated with two factors - \( \mu_2 \) and \( \mu_{11} \). The factor \( \mu_2 \) accounts for the decrease of the intensity of the incident beam caused by the reduction of purely elastically scattered electrons; and the factor \( \mu_{11} \) accounts for the increase of the intensity of the incoming beam caused by the contribution of the inelastically scattered electrons. The total intensity of the incident beam is conserved, therefore \( \mu_2 \) and \( \mu_{11} \) are associated
Figure 7.5: a) The calculated $\mu_{11}(r = r')$ for single silicon atom with the energy loss of 16 eV at 20 kV. b) The calculated $\mu_{11}(r = r')$ for a silicon lattice with the energy loss of 16 eV at 20 kV.
with each other, and the magnitude of both indicates the strength of the interference between the inelastically scattered waves. The calculation of $\mu_2$ and $\mu_{11}$ involves 4D Fourier transform of the MDFF. In order to decompose the 4D FT as combinations of 2D Fourier transforms, we have derived an approximation (Appendix D) based on the Wentzel model up to a resolution of 1 Å$^{-1}$. Our approximation can be conveniently applied for image calculations and optimized for different imaging conditions.

We calculated zero-loss filtered and plasmon-filtered images for the SALVE II microscope, based on the experimental EELS spectra obtained from the SALVE I microscope. According to our calculations for 20 kV, even for an one-atom thin structure like graphene, although only less than 1% of the electrons are inelastically scattered, the strong interference of these inelastically scattered waves results in dramatic decrease of the zero-loss filtered image intensity to 72%, compared with the case considering pure elastic scattering. For the thicker structure Si(110) (17 nm thick), 57% of the electrons are inelastically scattered, however the zero-loss filtered image intensity drops only to 60% compared with the case considering pure elastic scattering. The examples show that especially for low-Z materials such as carbon-based structures, the interference between the inelastically scattered waves dominates the image intensity. Our two examples clearly show that in general the influence of inelastic scattering cannot be neglected at 20 kV. The analysis on the zero-loss and plasmon-loss filtered images shows that the $C_e$—corrected plasmon-loss filtered images preserve the elastic contrast.
In order to achieve the highest resolution in \( C_s/C_c \)-corrected TEM images, high electron doses are required which only a few samples can withstand. Experimental HRTEM images are recorded with finite electron dose. In this chapter we perform dose-dependent HRTEM image calculations, and study the dependence of signal-to-noise ratio (SNR), atom contrast and resolution on electron dose and sampling. We introduce dose-dependent contrast, which is used to evaluate the visibility of objects under different dose conditions. Based on our calculations, we determine optimum samplings for high and for low electron dose imaging conditions.

We utilize the elastic model (Eqs. (3.1)-(3.3)) in the image calculation for graphene at low voltages ranging from 20 kV to 80 kV on a \( C_s/C_c \)-corrected microscope. The finite electron dose is taken into account based on Sec. 3.3 and the procedure is divided into two steps:

1. Determine the average number of electrons per image pixel;

2. Determine the actual number of electrons per image pixel based on Poisson statistics.

The average number of electrons collected by each detector pixel (Eq. (3.21)) depends on the electron dose, the sampling and the probability of the electron to be found on each pixel, which is the squared modulus of the image wave. We can obtain the probability distribution directly from the images calculated following Eqs. (3.1)-(3.3). The actual number of electrons can be generated with random Poisson distribution based on the average numbers.

Inelastic scattering is not included for the following reason:

On a \( C_e \)-corrected microscope, the contrast delocalization caused by inelastic scattering in a single layer of graphene at voltages as low as 20 kV is negligible. The influence of inelastic scattering on the image is mainly the decrease of the intensity contributed by the elastic scattered electrons (Chap. 7).

Parameters of the SALVE II microscope used for the image calculations are listed in Tab. 8.1. The defocus \( \Delta f \) and the coefficient \( C_s \) of the third-order spherical aberration are free parameters; \( C_5 = 4 \text{ mm}, C_e = 0 \) and residual focus spread \( \sigma(C_1) = 5 \text{ Å} \) are fixed.

\[ \text{This chapter is adapted based on [77].} \]
CHAPTER 8. IMAGE CALCULATION WITH FINITE DOSE

Table 8.1: Aberration parameters and image spread used for the simulation of images at an accelerating voltage of 20 kV, 40 kV, 60 kV and 80 kV on the $C_s/C_c$-corrected SALVE II microscope. The usable aperture determined by the maximum size of the usable phase plate is 50 mrad. $C_s$ is the coefficient of the third-order spherical aberration; $\Delta f$ is the defocus and $\sigma(C_s)$ represents the standard deviation of image spread. Reproduced from Ultramicroscopy with the reference [77].

<table>
<thead>
<tr>
<th>$HT$ (kV)</th>
<th>$C_s$ ($\mu$m)</th>
<th>$\Delta f$ (Å)</th>
<th>$\sigma(C_s)$ (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>-13</td>
<td>98</td>
<td>47</td>
</tr>
<tr>
<td>40</td>
<td>-12</td>
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<td>40</td>
</tr>
<tr>
<td>60</td>
<td>-11.5</td>
<td>72</td>
<td>29</td>
</tr>
<tr>
<td>80</td>
<td>-11.5</td>
<td>70</td>
<td>26</td>
</tr>
</tbody>
</table>

for all accelerating voltages. In the following sections we will evaluate the dependence of SNR (Sec. 8.1), atom contrast (Sec. 8.2) and specimen resolution (Sec. 8.3) on dose and sampling step by step. Based on these studies, we will determine the optimum sampling for imaging condition with finite dose in Sec. 8.4.

8.1 Dependence of SNR on dose and sampling

Fig. 8.1a) and b) show the evolution of the object visibility with respect to the sampling and dose, respectively. Each column corresponds to a specific sampling, and each row corresponds to a specific electron dose. Fig. 8.1c) is the low-pass filtered images of the ones in a) and the size of the low-pass filters are determined by the information limit, which depends on all damping functions. In Fig. 8.1a), as the sampling gets finer from left to right, the object visibility ameliorates first, then deteriorates. The object visibility increases with the dose in every column from bottom to top. The influence of the camera MTF can be ignored for sampling finer than 0.15 Å/pixel (green lines in CTF plot), since in these cases the MTF is always 1 covering the range of spatial frequency marked. For the $C_s/C_c$-corrected SALVE II microscope at 80 kV, the damping of the image spread function (yellow line) is much stronger than the damping of the focus spread function (red line).

Fig. 8.2a) shows that the SNRs of the calculated images (Fig. 8.1a)) increase with respect to the dose linearly at logarithmic scale for doses smaller than $5 \times 10^6$ e$^-$/nm$^2$, and converge gradually towards the maximum SNRs obtained for infinite dose. For coarse sampling, the maximum SNR is larger than for fine sampling. The behavior in Fig. 8.2a) can be understood by discussing Eqs. (3.22) and (3.24). Under low-dose conditions, since the number of electrons on each image pixel $D\delta^2 I_j$ is close to the average $\bar{D}\bar{\delta}^2 \bar{I}_j$, we can replace Pois($D\delta^2 I_j$) with Pois($D\bar{\delta}^2 \bar{I}$) and obtain

$$\sigma(N) \approx \sqrt{\frac{1}{J} \sum_{j=1}^{J} [\text{Pois}(D\delta^2 I_j) - \text{Pois}(D\bar{\delta}^2 \bar{I})]^2} \approx \sqrt{\frac{1}{J} \sum_{j=1}^{J} [\text{Pois}(D\bar{\delta}^2 \bar{I}) - \text{Pois}(D\bar{\delta}^2 \bar{I})]^2} = \sqrt{D\bar{\delta}^2 \bar{I}} = \sqrt{\bar{N}}, \quad (8.1)$$

$$\text{SNR} = \frac{N}{\sigma(N)} \approx \sqrt{D\bar{\delta}^2 \bar{I}} = \sqrt{\bar{N}}. \quad (8.2)$$

Therefore log(D) and log(SNR) show a linear dependence with the slope of 1/2 in the
Figure 8.1: (a) Calculated 80 kV HRTEM images of graphene for different doses and samplings with a usable aperture of 50 mrad. The last row in (a) shows the CTF for different samplings. The PCTF function (blue), focus spread envelope (red) and image spread envelope (yellow) are the same for each column. The MTF (green) depends on the sampling and in order to minimize the damping of MTF on the image contrast for graphene, samplings finer than 0.15 Å/pixel is required. The total CTF (purple) is a product of all the functions mentioned above. All images are displayed with the maximum contrast, namely the image intensities are mapped on the full grayscale values ranging between 0 and 255. Vertical dashed lines in the plots show the maximum spatial frequency achievable for the sampling written above. Reproduced from Ultramicroscopy with the reference [77].
Figure 8.1: (b) Sharp-cutoff low-pass filtered images of a). The radius of the low-pass filter applied for each image is determined by the information limit, which depends on the PCTF and all damping functions (CTF plots in a). Reproduced from Ultramicroscopy with the reference [77].
8.2. DEPENDENCE OF ATOM CONTRAST ON DOSE AND SAMPLING

low-dose region. Under high-dose conditions, \( \text{Pois}(D\delta^2I_j) \approx D\delta^2I_j \) and we obtain

\[
\sigma(N) = \sqrt{\frac{1}{J} \sum_{j=1}^{J} [\text{Pois}(D\delta^2I_j) - \text{Pois}(D\delta^2\bar{I}_j)]^2}
\approx \sqrt{\frac{1}{J} \sum_{j=1}^{J} [D\delta^2I_j - D\delta^2\bar{I}_j]^2} = D\delta^2\sigma(I), \tag{8.3}
\]

\[
\text{SNR} = \frac{\bar{N}}{\sigma(N)} \approx \frac{D\delta^2\bar{I}}{D\delta^2\sigma(I)} = \frac{\bar{I}}{\sigma(I)} = \text{const.} \tag{8.4}
\]

Here \( \sigma(I) \) is the standard deviation of the image calculated with infinite dose and \( \bar{I} \approx 1 \).

Fig. 8.2) evaluates as can be seen from Fig. 8.1b), that after low-pass filtering, the average SNR of the images are generally improved. Finer sampling results in more remarkable improvement. For the sampling of 0.15 Å/pixel and 0.01 Å/pixel with the electron dose of \( 1 \times 10^6 \text{e}^-/\text{nm}^2 \), the average SNR increase by factors of 1.8 and 23 after the low-pass filtering, respectively. However, the SNR is not directly related to the visibility of the images. For coarse sampling such as the 1st column in Fig. 8.1b), the image visibility is rather poor, but the SNR is above 10, higher than in the other cases (Fig. 8.2b)).

8.2 Dependence of atom contrast on dose and sampling

Contrast originates from the brightness difference between the object and the background. For the measurement of the experimental atom contrast, the intensities of the peak and valley: \( I_a \) and \( I_b \) are determined from a line profile drawn through the atoms, and the atom contrast is judged with either the modified Weber formula (Eq. (6.1)) or with the Michelson formula \[112\]

\[
C_M = \frac{I_a - I_b}{I_b + I_a}. \tag{8.5}
\]

In the case of very high electron dose, these formulas are correct because the SNR of the images are high enough so that the disturbance introduced by the electron noise to the image contrast is negligible. However, in an experimental image recorded with low dose, due to the strong statistical fluctuation of the electron counts in the neighbour pixels, the recognition of the object is degraded. This statistical influence is not included in Eq. (6.1) or Eq. (8.5), and the contrast value calculated based either on Eq. (6.1) or Eq. (8.5) can result in similar contrast values for both high-dose and low-dose images. Fig. 8.3 shows an example. Fig. 8.3a) and b) are extracted from Fig. 8.1 at the sampling of 0.038 Å/pixel. The intensity difference between the atoms and the background in Fig. 8.3a) (calculated with the dose of \( 1 \times 10^6 \text{e}^-/\text{nm}^2 \)) is lower than in b) (calculated with infinite dose), therefore the atom visibility in a) is lower than in b). However, the contrast evaluation based on the corresponding line profiles c) and d) with Eq. (6.1) or Eq. (8.5) produces similar values for both images, which is counter to our visual cognition.

In order to describe the statistical fluctuation in the experimental images, we introduce the term \( \sigma(N)/[\bar{N}\sigma(I)] \). Here \( \sigma(N) \) is the standard deviation of the image...
Figure 8.2: Average SNR as a function of the electron dose and sampling based on Fig. 8.1 a) unfiltered, b) sharp-cutoff low-pass filtered 80 kV HRTEM images calculated as a dependence on dose and sampling. Reproduced from Ultramicroscopy with the reference [77].
8.2. DEPENDENCE OF ATOM CONTRAST ON DOSE AND SAMPLING

Figure 8.3: The atom visibility in the image a) calculated with the electron dose of \(1 \times 10^6\) e\(^{-}/\text{nm}^2\) is drastically lower than in b) calculated with infinite dose. However, the conventional methods (Eqs. (6.1) and (8.5)) for measuring the atom contrast based on line profiles c) and d) produce similar results for the atom contrasts in a) and b). Both images are extracted from Fig. 8.1 for the sampling of 0.038 Å/pixel. The green line in c) is a smoothed profile of the line profile in a). Reproduced from Ultramicroscopy with the reference [77].
calculated with finite electron dose, and \( \bar{N} \sigma(I) \) is the standard deviation of the image \( I \) calculated with infinite dose (\( I \approx 1 \)) scaled by the average number of electrons per pixel \( \bar{N} \). Based on the discussion in Sec. 8.1, \( \sigma(N)/[\bar{N} \sigma(I)] \) is approximately proportional to \( 1/[\sqrt{DI\delta \sigma(I)}] \) under low-dose imaging conditions, and converges towards 1 for high-dose imaging conditions. The trend is confirmed by Fig. 8.4. As a result, the influence of the statistical fluctuation introduced by Poisson noise is smaller under high doses than under low doses, and smaller for coarse samplings than for fine samplings, generally.

Figure 8.4: The term \( \log[\sigma(N)/(\bar{N} \sigma(I))] \) decreases linearly with respect to \( \log(D) \) in the low-dose region, and converges towards 1 in the high-dose region. At fixed dose, the value of \( \sigma(N)/[\bar{N} \sigma(I)] \) for coarse sampling is generally smaller than for fine samplings. The only exception is the sampling 0.6 Å/pixel, where due to the strong damping of the MTF caused by coarse sampling, \( \sigma(I) \) is too small, resulting in \( \sigma(N)/[\bar{N} \sigma(I)] \) larger than in the case of 0.3 Å/pixel and 0.15 Å/pixel. Reproduced from Ultramicroscopy with the reference [77].

We evaluate the dose-dependent contrast by making one change to Eq. (6.1) and define the new dose-dependent contrast as

\[
\begin{align*}
C_d &= \frac{I_b - I_a}{[\sigma(N)/\bar{N} \sigma(I)]^\kappa I_b} = \frac{I_b - I_a}{I_b} \left[ \frac{\bar{N} \sigma(I)}{\sigma(N)} \right]^\kappa = C_W [SNR \cdot \sigma(I)]^\kappa. \\
&= (8.6)
\end{align*}
\]

A factor \( [\sigma(N)/[\bar{N} \sigma(I)]^\kappa \) is introduced to the denominator of Eq. (6.1). Here \( \kappa \) is a positive factor to be determined, and based on Appendix F we obtain \( \kappa \approx 2 \) for all samplings. The introduction of this term originates from the relation between \( \sigma(N)/[\bar{N} \sigma(I)] \) and atom contrast (Figs. 8.1a) and 8.4). The term \( \sigma(N)/[\bar{N} \sigma(I)] \) decreases with respect to the dose, resulting in increased atom contrast. For images calculated with very high dose, \( \sigma(N)/[\bar{N} \sigma(I)] \) converges to 1 and the atom contrast converges to Eq. (6.1), which is the contrast calculated for infinite dose. For low dose, the term \( \sigma(N)/[\bar{N} \sigma(I)] \) is approximately proportional to \( 1/[\sqrt{\bar{N} \sigma(I)}] \), and \( C_d \) approaches 0 when \( \bar{N} \) or the dose \( D \) approaches 0. The trend is consistent with what we observe in Fig. 8.1b.)
8.2. DEPENDENCE OF ATOM CONTRAST ON DOSE AND SAMPLING

Figure 8.5: Atom contrast as a function of the electron dose and sampling at 80 kV. a) corresponds to Fig. 8.1a) and b) corresponds to Fig. 8.1b). The atomic resolution of 1.4 Å for graphene is obtained with the lowest dose of $5 \times 10^6$ e$^-$/nm$^2$ at the sampling of 0.15 Å/pixel and 0.075 Å/pixel ((Fig. 8.6a)), and in this case the maximum contrast of 8.6% is obtained under the sampling of 0.15 Å/pixel, marked by the dashed lines. After low-pass filtering, the atom contrast under the same dose is improved to 13%. Reproduced from Ultramicroscopy with the reference [77].
Figure 8.6: Specimen resolution as a function of electron dose and sampling at 80 kV. (Smaller value corresponds to better resolution.) a) corresponds to Fig. 8.1(a) and b) corresponds to Fig. 8.1(b). Low-pass filtering improves the specimen resolution for fine samplings under low-dose conditions. For single-layer graphene, the atomic resolution can be achieved at 1.4 Å, marked by the dashed lines in a) and b). The lowest dose to achieve this resolution is $5 \times 10^6$ e$^-$/nm$^2$ for an unfiltered image, and $2 \times 10^6$ e$^-$/nm$^2$ for a low-pass filtered image. Reproduced from Ultramicroscopy with the reference [77].
Fig. 8.5 shows the atom contrast calculated with Eq. (8.6) for different samplings and electron doses. These curves are now in agreement with our visual cognition. As the electron dose increases, the atom contrast improves until it reaches the upper limit. For coarse sampling, the maximum atom contrast as well as the dose required to reach this maximum value is smaller than for fine sampling. The maximum contrast is 9.4% for the sampling of 0.3 Å/pixel, 14.7% for the sampling of 0.15 Å/pixel, 16.6% for the sampling of 0.075 Å/pixel and 17.2% for the samplings finer than 0.038 Å/pixel. Low-pass filtering (Fig. 8.5b) can enhance the atom contrast (compared with Fig. 8.5a) and the effect is especially remarkable for fine samplings.

The distance between two neighbour atoms in graphene is 1.4 Å, and this resolution can be obtained with the lowest dose of $5 \times 10^6 \text{ e}^-/\text{nm}^2$ at the sampling of 0.15 Å/pixel and 0.075 Å/pixel (Fig. 8.6a)). The dashed line in Fig. 8.5a) shows the maximum atom contrast of 8.6% obtained under this dose condition. Low-pass filtering not only results in atomic resolution at fine samplings $\leq 0.075$ Å/pixel (Fig. 8.6b)), but also improves the atom contrast (Fig. 8.5b)). At the sampling of 0.15 Å/pixel under the dose of $5 \times 10^6 \text{ e}^-/\text{nm}^2$, the contrast is improved to 13%.

### 8.3 Dependence of specimen resolution on dose and sampling

The attainable specimen resolution $d_s$ is dependent on the electron dose $D$, SNR and the dose-dependent contrast $C_d$. We adapt Eq. (3.1) of [113] to include the new dose-dependent contrast and express the specimen resolution as

$$
 d_s = \sqrt{d_i^2 + \frac{(\text{SNR})^2}{C_d^2 D}}.
$$

Here $d_i$ is the instrumental resolution, which is mainly defined by the wavelength $\lambda$ and the usable aperture $UA$: $d_i = \lambda/UA$.

Eq. (8.7) indicates that specimen resolution is a function of the electron dose $D$ and sampling, since SNR and $C_d$ depend on the two quantities. The specimen resolution $d_s$ improves as the electron dose increases, and reaches the limit of instrumental resolution for infinite dose. Based on the calculations for SNR (Sec. 8.1) and atom contrast (Sec. 8.2), we plot the specimen resolution with respect to dose and sampling in Fig. 8.6. The specimen resolution approaches infinity for very low doses, at which the atom contrast is also close to 0 (Fig. 8.5). The specimen resolution improves as the dose increases, and converges towards 0.8 Å which is the instrumental resolution at 80 kV on the SALVE II microscope.

Low-pass filtering effectively improves the specimen resolution for fine samplings under low dose conditions. For single-layer graphene, the atomic resolution can be achieved at 1.4 Å, marked by the dashed lines in Fig. 8.6a) and b). The lowest dose to achieve this resolution is $5 \times 10^6 \text{ e}^-/\text{nm}^2$ with the sampling of 0.15 Å/pixel or 0.075 Å/pixel for unfiltered images, and $2 \times 10^6 \text{ e}^-/\text{nm}^2$ with the samplings $\leq 0.075$ Å/pixel for the low-pass filtered cases.

### 8.4 Determination of the optimum sampling

In order to obtain good object visibility under low dose conditions, it is necessary to choose a suitable sampling. Coarse sampling causes both contrast and resolution loss,
and hyperfine sampling results in poor contrast (see Fig. 8.5 and 8.6).

Generally, it is enough to resolve the sample structure up to the required specimen resolution $d_s$. The highest spatial frequency corresponding to the specimen resolution is $1/d_s$, which is smaller than or equal to the instrumental resolution $1/d_i$. It should be guaranteed that the Nyquist frequency $q_N \geq 1/d_s$, so that the sampling $\delta$ satisfies $\delta = 1/(2q_N) \leq d_s/2$, based on the sampling theorem for discrete Fourier transform [114].

On the other hand, the damping of the detector MTF at the Nyquist frequency $q = q_N$ is so strong that the contrast corresponding to this frequency is only 10-15% compared with the case without any MTF damping (see Fig. E.1 in the Appendix E). Coarse sampling results in strong damping of the MTF and accordingly weak atom contrast. This effect can be confirmed under high dose conditions ($> 5 \times 10^9 \text{ e}^-/\text{nm}^2$), shown in Fig. F.2 in Appendix F which is an extended version of Fig. 8.5a) by exhibiting a broader range of electron dose - As the sampling gets coarse, the maximum atom contrast decreases. At the sampling of 0.6 Å/pixel, the atom contrast obtained with even infinite electron dose is only about 1%.

The influence of the MTF damping on the image contrast can also be confirmed for low-pass filtered images (Fig. 8.5)). The filtered atom contrast for coarse sampling is lower than for fine sampling under the same dose condition.

For both unfiltered and filtered images, fine sampling ($\leq 0.075$ Å/pixel) is necessary for obtaining high atom contrast and an ideal MTF profile requires $\text{MTF} \approx 1$ covering the spatial frequency up to the required specimen resolution, indicating that $(1/d_s)/(2q_N) \leq 0.1$. Therefore the sampling should be

$$\delta = 1/(2q_N) \leq 0.1d_s. \quad (8.8)$$

The maximum sampling also defines the lowest magnification ratio allowed:

$$M = \frac{\delta_p}{\delta} \geq 10\delta_p/d_s. \quad (8.9)$$

Here $\delta_p$ is the physical size of the detector pixel. If one wants to obtain an image with a magnification ratio larger than $10\delta_p/d_s$, then the sampling $\delta$ should satisfy the relation $\delta \leq \delta_p/M$.

In order to obtain the maximum atom contrast for experimental images, the sampling should be finer than 0.075 Å/pixel and the required dose should be larger than $5 \times 10^9 \text{ e}^-/\text{nm}^2$ according to Fig. F.2. However, such high electron dose is not realistic for beam-sensitive materials in TEM, which also indicates that it is barely possible to obtain an experimental image with the maximum atom contrast. For imaging with finite dose, the atom contrast obtained with fine sampling is not necessarily higher than obtained with coarse sampling under the same dose conditions. An example is shown in Figs. 8.5 and F.2 where the atom contrast at the sampling of 0.15 Å/pixel is higher than at finer samplings $\leq 0.075$ Å/pixel for the electron doses between $5 \times 10^6 \text{ e}^-/\text{nm}^2$ and $1 \times 10^7 \text{ e}^-/\text{nm}^2$.

In order to find out the best sampling under low-dose conditions, we substitute $C_d = C_W[\text{SNR} \cdot \sigma(I)]^2$ (Eq. 8.6) and the approximation $\text{SNR} \approx \sqrt{N}$ (Eq. 8.2) into
the second term in Eq. (8.7). We obtain
\[
\frac{(SNR)^2}{C_d^2D} = \left[ \frac{1}{C_W \sigma^2(I)} \right]^2 \frac{1}{ND} = \left[ \frac{1}{\delta C_W \sigma^2(I)} \right]^2 \frac{1}{D^2I}.
\] (8.10)

We define
\[
G(\delta) = \left[ \frac{1}{\delta C_W \sigma^2(I)} \right]^2,
\] (8.11)
and since \(C_W\) as well as \(\sigma(I)\) depends on the sampling \(\delta\), \(G(\delta)\) is an exclusive function of \(\delta\). In order to achieve the required specimen resolution \(d_s\) with low electron dose \(D\), \(G(\delta)\) must be small enough. If \(G(\delta)\) reaches the minimum, then so does the required dose \(D\).

In our case for graphene imaged with the SALVE II microscope, \(G(\delta)\) is plotted with respect to the sampling \(\delta\) in Fig. 8.7 for different accelerating voltages. Fig. 8.7 shows that \(G(\delta)\) reaches the minimum for all accelerating voltages around the sampling of 0.2 Å/pixel, indicating that the required electron dose to achieve a specific resolution at this sampling is the lowest with the current experimental settings. The closest sampling in our examples is 0.15 Å/pixel. On the other hand, a fine specimen resolution under a given dose condition also indicates a large contrast value \(C_d\) under this condition (Eq. (8.7)).

In the case of graphene, the distance between two neighbour atoms is 1.4 Å. As shown in Fig. 8.6a), the lowest electron dose to achieve this atomic resolution is \(5 \times 10^6\) e\(^-\)/nm\(^2\) at the sampling of 0.15 Å/pixel or 0.075 Å/pixel, and the maximum contrast of about 8.6% under this dose condition is obtained at the sampling of 0.15 Å/pixel, which is consistent with the analysis above.

As a summary, the optimum sampling and the lowest magnification ratio for a raw experimental image recorded with high electron dose are determined by the required specimen resolution \(d_s\):
\[
\delta = \min\{0.1d_s, \frac{\delta_p}{M}\} \quad (d_s \geq d_i, \ M \geq 10\delta_p/d_s).
\] (8.12)

For unknown samples, the required specimen resolution cannot be determined and one tends to record the images up to the instrumental resolution of the microscope. In this case the optimum sampling is determined by replacing \(d_s\) with \(d_i\) in Eq. (8.12).

For experimental images recorded with low electron dose, the optimum sampling is determined by the minimal value of Eq. (8.11). In order to improve the contrast of the low-dose images, low-pass filters can be applied. If one wants to obtain the maximal atom contrast in a low-pass filtered image recorded with low dose, fine sampling \(\leq 0.075\) Å/pixel is required.

8.5 A comparison between the calculation and the experiment at 80 kV

A focal series (defocus step size 0.53 nm) with spherical aberration close to zero (0±4 µm) was recorded on the GIF camera (Gatan model US1000) with 2048 × 2048 pixels on the Titan microscope operated at 80 kV. Due to the 20× post-magnification of the GIF camera, extremely high spatial sampling of 40 pixels per Angstrom was achieved for a small region of the sample. In this way, we minimized the damping of the camera
CHAPTER 8. IMAGE CALCULATION WITH FINITE DOSE

Figure 8.7: The plot of $G(\delta) = 1/[\delta C W \sigma^2(I)]^2$ with respect to the sampling $\delta$ for 20 kV, 40 kV, 60 kV and 80 kV on the current $C_s/C_c$-corrected SALVE II prototype. The usable aperture is 50 mrad, and parameters for calculations are listed in Tab. 8.1. At the sampling of 0.2 Å/pixel, $G$ reaches the minimum, indicating that the electron dose $D$ required to reach the resolution $d_s$ also reaches the minimum. Reproduced from Ultramicroscopy with the reference [77].

MTF (Chap. 8). At this sampling, the absolute atom contrast obtained with infinite electron dose ($C = |I_b - I_a|/I$) is -8.9% for bright atom contrast and 8.7% for dark atom contrast (see Fig. 6.2 right column). The standard deviation of the calculated image is $\sigma(I) = 0.025$ for both bright atom contrast and dark atom contrast.

The electron dose applied for the experiment is about $7.9 \times 10^6$ e$^-$/nm$^2$, namely 50 e$^-$/pixel based on the sampling. The experimental images were first processed with low-pass filtering with the cut-off radius the same as the usable aperture, which includes the first reflections of graphene. Then the contrasts of the filtered images were measured for each defocus value averaging over the visible unit cells in the contamination-free area based on Eq. (6.1). Several filtered experimental images are shown in Fig. 8.8 together with the measured contrast vs. defocus plot. In the experimental contrast vs. defocus plot, all contrasts are given as absolute values. The negative (bright atom) contrast is present from roughly 0 to 7 nm defocus. Zero defocus is assigned at the contrast minimum where also the contamination contrast vanishes.

In the curve for filtered images, we find a maximum contrast of 8.5% for bright-atom condition (defocus +2.6 nm) and 8.4% as the dark-atom maximum (defocus -3.7 nm). The contrast values are nearly identical. The standard deviation of the corresponding unfiltered image is $\sigma_{exp}(N) = 3.94$ for bright atom contrast and $\sigma_{exp}(N) = 4.01$ for dark atom contrast. Based on Eq. (8.6), the maximum contrast of the unfiltered images is -0.88% for bright atom imaging and 0.83% for dark atom imaging.

In order to compare the experiment with the calculation, we have calculated the images with the given dose, and the standard deviation of the image is 3.81 for bright atom contrast and 3.89 for dark atom contrast, which are comparable with the experiments.
Based on Eq. (8.6) the atom contrast under this dose condition should be -0.94% for bright atom contrast and 0.88% for dark atom contrast.

The calculated and experimental images are shown in Fig. 8.9. On the right column the line profiles for the two cases are presented. Based on the line profiles for unfiltered and filtered images, the experimental and calculated results are consistent with a sufficient degree of accuracy.

Figure 8.8: Absolute atom contrast at 80 kV and Cs ~ 0 µm for single-layer graphene as a function of defocus. Note that the images measures only about 20 unit cells in diameter but were recorded with the full 2048×2048 pixels resolution of the CCD camera. Due to this extremely high oversampling (40 pixels per angstrom), we obtain 8 – 9% contrast for single-layer graphene (At a more common sampling of ~ 5 pixel per angstrom, the contrast is ca. 2× smaller; in agreement with a measured camera MTF [115]). As predicted by calculation, the maximum contrasts for bright atom and dark atom conditions are nearly identical. (Scale bar : 1nm). Reproduced from Ultramicroscopy with the reference [74].

8.6 Conclusions

In this chapter we have studied the influence of electron dose and sampling on the SNR, dose-dependent contrast and resolution using dose-dependent HRTEM image calculations. All three quantities improve with increasing electron dose, converging towards their values obtained under infinite dose condition. As the sampling gets coarse, the SNR increases and the resolution decreases; the atom contrast improves as long as the damping of the detector MTF is negligible.

We have determined the optimum sampling for high-dose and low-dose conditions, respectively. Under high-dose conditions, the optimum sampling depends mainly on the required specimen resolution; under low-dose conditions, the optimum sampling is determined by our criteria that the required specimen resolution should be achieved with the minimal electron dose.

We have analysed the 80 kV HRTEM images of graphene and found good qualitative agreement between the experimental images of given dose and our dose-dependent image calculations.
We have also shown that low-pass-filtering improves both, the SNR of the image and the atom contrast, which as a result, effectively reveals information hidden in a low-dose high-resolution TEM image.

Figure 8.9: The comparison between the calculated images and experimental HRTEM images recorded on Titan microscope operated at 80 kV. Left column: The calculated image with the effective dose of $7.9 \times 10^6 \text{ e}^-/\text{nm}^2$ and the sampling of 0.025 Å/pixel for bright and dark atom imaging conditions. Middle column: The experimental images with the effective dose of $7.9 \times 10^6 \text{ e}^-/\text{nm}^2$ and the sampling of 0.025 Å/pixel. Right column: the line profiles marked in the images shown in the left and middle columns. The corresponding filtered images and the smoothed profiles are presented in the last two rows. One can see that the calculation and experiment match within the error margin of 6%.
Part IV

Summary
The whole work has systematically studied the influence of elastic and inelastic scattering as well as electron dose on the HRTEM image contrast. Elastic model based on the Wentzel potential has been testified for HRTEM images of graphene at 80 kV and 20 kV (Chap. 6). For the first time, we calculate the image intensity by averaging over the energy distribution of the elastically scattered imaging electrons, derived from the experimental EELS data.

Based on the study, significant improvement of contrast can only be achieved by the additional correction of chromatic aberration as well as the elimination of other damping effects like image spread. Moreover, we show that a further increase of contrast is possible by using bright atom imaging conditions, even for a single layer of atoms. Our calculations clearly show that even graphene cannot be treated as a weak phase object at an accelerating voltage of 20 kV. In other words, all atoms are strong scatterers at voltages smaller than about 20 kV.

In Chap. 7 the influence of inelastic scattering for graphene imaged at 20 kV has been presented by utilizing the mutual coherence approach. We calculated zero-loss filtered and plasmon-loss filtered images for the SALVE II microscope, based on the experimental EELS spectra obtained from the SALVE I microscope. According to our calculations for 20 kV, even for a one-atom thin structure like graphene, although only less than 1% of the electrons are inelastically scattered, the strong interference of these inelastically scattered waves results in dramatic decrease of the zero-loss filtered image intensity to 72%, compared with the calculation for pure elastic scattering. For the 17 nm thick structure Si⟨110⟩, as much as 57% of the electrons are inelastically scattered, however the zero-loss filtered image intensity drops only to 60% compared with the calculation for pure elastic scattering. The examples show that especially for low-Z materials such as carbon-based structures, the interference between the inelastically scattered waves dominates the image intensity. Our two examples show that in general the influence of inelastic scattering cannot be neglected at 20 kV. The analysis on the zero-loss and plasmon-loss filtered images shows that the Cc—corrected plasmon-loss filtered images preserve the elastic contrast.

Chap. 8 has discussed the influence of the electron dose and sampling on the SNR, atom contrast and resolution using dose-dependent HRTEM image calculations. We have introduced a modified contrast definition accounting for object visibility by taking into account the electron dose. All three quantities improve with increasing electron dose, converging towards their values obtained under infinite dose condition. As the sampling increases (gets coarse), the SNR increases, but the resolution decreases. The atom contrast improves as long as the damping of the detector MTF is negligible. We have determined the optimum sampling for high-dose and low-dose conditions, respectively. Under high-dose conditions, the optimum sampling depends mainly on the required specimen resolution; under low-dose conditions, the best sampling is determined by our criteria that the required specimen resolution should be achieved with the minimal electron dose.

We have analysed the 80 kV experimental HRTEM images of graphene based on the new definition of contrast which considers the finite electron dose. We found good qualitative agreement between the experimental and calculated images. Low-pass filtering improves both the SNR of the image and the atom contrast, which as a result, effectively reveals information hidden in a high-resolution TEM image recorded with low dose.
Part V

Appendix
Appendix A

Liouville-Neumann-Born series

Non-relativistic time-independent Schrödinger equation Eq. (2.3) can be written as

\[(\nabla^2 + k_0^2)\Psi(r) = \frac{2m_e}{\hbar^2} V(r)\Psi(r).\] (A.1)

In order to solve the differential equation, one can implement Green’s function \(G(r, r')\) and transform the differential equation into integral equation. The solution consists of a general solution \(e^{ik_0r}\) and a special solution, which is written as

\[\Psi(r) = e^{ik_0r} + \frac{2m_e}{\hbar^2} \int G(r - r')V(r')\psi(r')d^3r',\] (A.2)

with the Green’s function satisfying

\[(\nabla^2 + k_0^2)G(r - r') = \delta(r - r').\] (A.3)

Performing Fourier transform on both sides of Eq. (A.3) and employing the property of Fourier transform

\[\text{FT} \left[\frac{d^n G(r)}{dr^n}\right] = (iq)^n \hat{G}(q)\] (A.4)

we get

\[\hat{G}(q) = \frac{1}{k_0^2 - q^2}\] (A.5)

and

\[G(r - r') = \frac{1}{(2\pi)^3} \int \int \int \frac{e^{iq(r-r')}}{k_0^2 - q^2} d^3q\]

\[= \frac{1}{(2\pi)^2} \int_0^\infty \frac{q^2 dq}{k_0^2 - q^2} \int_0^\pi e^{iq|r-r'|\cos\theta} \sin\theta d\theta\]

\[= \frac{1}{4i\pi^2|r-r'|} \int_0^\infty \frac{q}{k_0^2 - q^2} (e^{iq|r-r'|} - e^{-iq|r-r'|}) dq\] (A.6)

\[= -\frac{1}{4i\pi^2|r-r'|} \int_{-\infty}^{+\infty} \frac{q e^{iq|r-r'|}}{(q + k_0)(q - k_0)} dq.\]
The integral Eq. (A.6) has two singularities at $q = -k_0$ and $q = k_0$, respectively. The physical meanings of the two signs are different - $e^{ik_0 r}$ represents outgoing wave and $e^{-ik_0 r}$ represents incoming wave. Since scattered wave is outgoing, we only have to take the singularity $q = k_0$ into account. Introducing $g(q) = \frac{qe^{iq|r-r'|}}{(q+k_0)(q-k_0)}$ and according to Fig. A.1 we have

$$\int_{-\infty}^{+\infty} \frac{qe^{iq|r-r'|}}{q+k_0} dq = \int_{-\infty}^{+\infty} g(q) dq = \int_{-\infty}^{+\infty} \frac{g(q)}{q-k_0} dq - \int_{A_{rc}} \frac{g(q)}{q-k_0} dq. \tag{A.7}$$

Based on Cauchy Integral Formula, the first integral in Eq. (A.7) results in

$$\int_{-\infty}^{+\infty} \frac{g(q)}{q-k_0} dq = 2\pi i f(k_0) = \pi ie^{ik_0 |r-r'|}. \tag{A.8}$$

The second integral in Eq. (A.7) is zero according to estimation lemma. In order to prove it, we introduce $q = Re^{i\theta}$ and $dq = iRe^{i\theta}d\theta$.

$$\int_{A_{rc}} g(q) dq = \int_{0}^{\pi} \frac{g(Re^{i\theta})}{Re^{i\theta}-k_0} iRe^{i\theta} d\theta \leq \int_{0}^{\pi} \left| \frac{g(Re^{i\theta})}{Re^{i\theta}-k_0} \right| |iRe^{i\theta}| d\theta$$

$$= \int_{0}^{\pi} \frac{R^2 e^{-R\sin \theta |r-r'|}}{R^2 \sqrt{1 - 2 \frac{k_0^2}{R^2} \cos 2\theta + \frac{k_0^4}{R^4}}} d\theta. \tag{A.9}$$

At the limit $R \to \infty$, the value of the square root converges towards 1. Eq. (A.9) reduces to

$$\int_{0}^{\pi} e^{-R \sin \theta |r-r'|} d\theta = 2 \int_{0}^{\pi/2} e^{-R \sin \theta |r-r'|} d\theta \leq 2 \int_{0}^{\pi/2} e^{-\frac{2R \theta |r-r'|}{\pi}} d\theta$$

$$= - \frac{\pi}{R |r-r'|} (e^{-R |r-r'|} - 1). \tag{A.10}$$

Eq. (A.10) converges to 0 at the limit $R \to \infty$; hence Eq. (A.6) ends in

$$G(r-r') = - \frac{e^{ik_0 |r-r'|}}{4\pi |r-r'|}. \tag{A.11}$$

The total wave therefore becomes

$$\Psi(r) = e^{ik_0 r} - \frac{m_e}{2\pi \hbar^2} \int V(r') \Psi(r') d^3r'. \tag{A.12}$$

In order to calculate $\Psi(r)$, one can implement iteration. The iterative series is called Liouville-Neumann-Born series, and its solution can be obtained by iteration. The first Born approximation is obtained by replacing $\Psi(r')$ by the incident wave $e^{ik_0 r'}$, and the second-order Born approximation is obtained by substituting the solution obtained with the first Born approximation for $\Psi(r')$ in Eq. (A.12).
Appendix B

Some quantities derived based on the Wentzel model

Screened Coulomb potential, also called Wentzel-Yukawa potential is used to describe the interaction between the nucleus and one electron [76]. The screening radius $a$ accounts for the range of Coulomb interaction. As the distance $r$ between the nucleus and the electron increases, the potential decays exponentially and the Coulomb potential of an electron $e/r$ is therefore effectively suppressed. The screened Coulomb potential is sufficient for the modelling of atomic potential if we neglect the inner-shell structure of the atom. The screened Coulomb potential energy adapts the form of

$$V(r) = -\frac{Ze^2 \exp(-r/a)}{r}. \quad (B.1)$$

where $Z$ is the atomic number, and $a = a_H Z^{-1/3}$ with the Bohr radius $a_H = 0.0529$ nm.

This part shows the some quantities derived based on the Wentzel model, including the elastic form factor, phase object approximation and the scattering cross-sections.

B.1 Elastic form factor

The concept of form factor is widely used for X-ray scattering, which is defined as the Fourier transform of the electron density $n_e$. The electron density is related to the potential, which corresponds to the electron-electron interaction, by Poisson’s equation:

$$\nabla^2 V_e(r) = -\frac{n_e(r)e}{\varepsilon_0}. \quad (B.2)$$

In the case of screened Coulomb potential, the potential corresponding to the electron-electron interaction equals the difference between the unscreened Coulomb potential and the screened potential:

$$V_e(r) = -\frac{Ze}{4\pi\varepsilon_0} \left[ \frac{1}{r} - \frac{\exp(-r/a)}{r} \right]. \quad (B.3)$$

Using the property of Fourier transform (Eq. (A.4)), we obtain from Eq. (B.2) 

$$K^2 FT[V_e(r)] = \frac{e}{\varepsilon_0} FT[n_e(r)] = \frac{e}{\varepsilon_0} F(K). \quad (B.4)$$
Therefore the form factor $F(K)$ can be calculated by substituting Eq. (B.3) into Eq. (B.4):

$$F(K) = \frac{ZK^2}{4\pi} \int \int \int \frac{1}{r} e^{-r/a} e^{-iKr} d^3r.$$  \hspace{1cm} (B.5)

The integral with respect to the first term in Eq. (B.5) results in $4\pi/K^2$. The second integral in Eq. (B.5) is evaluated as

$$\int \frac{1}{r} e^{-r/a} e^{-iKr} e^{-r/a} r d^3r = \frac{4\pi a^2}{1/K - iK}.$$  \hspace{1cm} (B.6)

Therefore we obtain the form factor $F(K)$:

$$F(K) = \frac{Z}{1 + K^2a^2}.$$  \hspace{1cm} (B.7)

**B.2 Phase object approximation**

By substituting Eq. (B.1) into Eq. (2.60), we obtain the projected potential based on Wentzel model:

$$\Phi(\rho) = -\frac{1}{\hbar^2} \int_{-\infty}^{+\infty} V(\rho, z)dz = \frac{Ze^2}{4\pi\varepsilon_0 \hbar c \beta} \int_{-\infty}^{+\infty} \exp\left(-\frac{r}{a}\right) r dz = \frac{Ze^2}{4\pi\varepsilon_0 \hbar c \beta} \int_{-\infty}^{+\infty} \exp\left(-\sqrt{\rho^2 + z^2}/a\right) d\rho.$$  \hspace{1cm} (B.8)

Introducing the Sommerfeld constant $\alpha_s = e^2/(4\pi\varepsilon_0 \hbar c)$ and $z = \rho \sinh t$, we obtain $dz = \rho \cosh t dt$ and $r = \rho / \sqrt{1 + \sinh^2 t}$. Eq. (B.8) becomes

$$\Phi(\rho) = \frac{Ze^2}{4\pi\varepsilon_0 \hbar c \beta} \int_{-\infty}^{+\infty} \exp\left(-\rho \cosh t/\alpha_s\right) \rho \cosh t dt = \frac{Ze^2}{4\pi\varepsilon_0 \hbar c \beta} \int_{-\infty}^{+\infty} \exp\left(-\rho \cosh t/\alpha_s\right) dt = \frac{2Ze^2}{\beta} K_0(\rho/\alpha_s).$$  \hspace{1cm} (B.9)

**B.2.1 Scattering cross section based on the first-order Born approximation**

According to Eq. (2.51), the scattering amplitude corresponding to Wentzel potential within the frame of the first Born approximation is

$$f(K) = C \int \int \int \frac{e^{-r/a}}{r} e^{-iKr} d^3r.$$  \hspace{1cm} (B.10)

Here $C = Ze^2 m_e/(8\pi^2 \hbar^2 \varepsilon_0)$. On the analogy of Eq. (B.6), we obtain

$$f(K) = C \frac{4\pi a^2}{1 + K^2a^2}.$$  \hspace{1cm} (B.11)
For small-angle scattering (Fig. 2.3), we obtain \( K = 2k_0 \sin(\theta/2) \); therefore Eq. (B.11) becomes

\[
f(\theta) = C \frac{4\pi a^2}{1 + 4k_0^2 a^2 \sin^2 \frac{\theta}{2}}.
\] (B.12)

Eq. (B.12) shows that for real potential with rotational symmetry, the scattering amplitude based on first-order Born approximation is a real quantity. For unscreened Coulomb potential, the corresponding scattering amplitude is

\[
f_{\text{uns}}(\theta) = C \frac{4\pi}{K^2} = C \frac{\pi}{k_0^2 \sin^2 \frac{\theta}{2}}.
\] (B.13)

Fig. B.1 shows the comparison of differential scattering cross-section calculated by \( d\sigma_{\text{el}}/d\Omega = |f(\theta)|^2 \) between screened and unscreened Coulomb potential. For unscreened potential, \( d\sigma_{\text{el}}/d\Omega \) approaches infinite at \( \theta = 0 \), which is avoided in the case of the screened potential.

![Figure B.1: Differential cross-section for elastic scattering calculated based on screened and unscreened Coulomb potential, exemplified by Au atom 20 kV. The screened Coulomb potential avoids infinity at \( \theta = 0 \).](image)

Based on Eq. (2.24), the elastic scattering cross-section within the frame of the first-order Born approximation is therefore

\[
\sigma_B = 2\pi \int_0^\pi |f(\theta)|^2 \sin \theta d\theta = 32\pi^3 C^2 a^4 \int_0^\pi \frac{1}{(1 + 4k^2 a^2 \sin^2 \frac{\theta}{2})^2} \sin \theta d\theta
\]

\[
= 32\pi^3 C^2 a^4 \int_0^\pi \frac{1}{[1 + 2k^2 a^2 (1 - \cos \theta)]^2} \sin \theta d\theta
\]

\[
= \frac{1}{\pi} \left( \frac{Z e^2 m_e a^2}{\hbar^2 \varepsilon_0} \right)^2 \frac{1}{1 + 4k^2 a^2}
\] (B.14)
B.2.2 Scattering cross-section based on the POA

Since the POA satisfies optical theorem (Eq. 2.70), we only have to calculate the imaginary part of the forward amplitude, in order to obtain the total scattering amplitude. Substituting Eq. (B.9) into Eq. (2.70), we obtain

\[
\sigma_P = \frac{4\pi}{k_0} \Im[f(0)] = 8\pi \int_0^\infty \sin^2 \frac{\Phi}{2} \rho d\rho
\]

\[
= 8\pi \int_0^\infty \sin^2 \frac{Z\alpha S K_0(\rho/a)}{\beta} \rho d\rho.
\]

(B.15)

For phase-object approximation, we can calculate the phase of \( f(\theta) \) by employing Eqs. (2.68) and (2.69). For Wentzel model we have

\[
\eta(\theta) = \arctan \frac{\Im[f(\theta)]}{Re[f(\theta)]}
\]

\[
= \arctan \frac{2 \int_0^\infty \sin^2 \frac{\Phi}{2} J_0(k\rho\theta) \rho d\rho}{\int_0^\infty \sin \Phi J_0(k\rho\theta) \rho d\rho}
\]

\[
= \arctan \frac{2 \int_0^\infty \sin^2 \frac{Z\alpha S K_0(\rho/a)}{\beta} J_0(k\rho\theta) \rho d\rho}{\int_0^\infty \sin 2 \frac{Z\alpha S K_0(\rho/a)}{\beta} J_0(k\rho\theta) \rho d\rho}.
\]

(B.16)
Appendix C

Image contrast based on the WPOA

To understand the differences of image contrast based on POA and WPOA, we present a short review of WPOA. Weak phase objects are generally considered to be very thin and to change the phase of the incident wave only up to the exit plane $z_e$. We assume that the illumination is parallel to the optic axis and the incident wave is plane wave; hence the resulting exit wave is given by Eq. (2.59).

$$
\psi_e(\rho) = e^{i\Phi(\rho)} = \exp[-\frac{i}{\hbar w} \int_{-\infty}^{z} V(\rho, z') dz'].
$$

(C.1)

Defining the interaction parameter $\sigma = 1/(\hbar w)$ and $V_p(\rho) = \int_{-\infty}^{z} V(\rho, z') dz'$, as well as assuming that the term $\sigma V_p \ll 1$, we can expand the exit wave in a Taylor series. The first two terms $1 + i\sigma V_p(\rho)$ give the so-called WPOA. The image intensity for fixed $\Delta E$ is therefore given by

$$
I_{\Delta E}(\rho) = 1 - 2\sigma FT^{-1}[A(q)V(q)\sin\chi(q, \Delta E)]p(\Delta E)d(\Delta E).
$$

(C.3)

The total image intensity has the standard form:

$$
I = \int I_{\Delta E}(r)p(\Delta E)d(\Delta E)
= 1 - 2\sigma \int FT^{-1}[A(q)V(q)\sin\chi(q, \Delta E)]p(\Delta E)d(\Delta E).
$$

(C.4)

The first term describes the background intensity. For a weak phase object, the background intensity is close to 1. The second term defines the phase contrast. The aperture function $A(q)$ mimics the effect of a beam-limiting aperture placed at the back-focal plane of the objective lens. The weighting function $p(\Delta E)$ describes the energy spread.

1This chapter is adapted based on [74].
of the scattered electrons. After correcting the chromatic aberration ($\chi_c = 0$), the phase $\chi = \chi_g$ reverses its sign when the signs of the geometrical aberrations $\chi_g$ are interchanged Eq. (3.15). In this case, the image contrast described by Eq. (6.1) changes its sign but not its absolute value.
Appendix D

The factorization of the MDFF\(^1\)

We have calculated \(S(K, K', \Delta E)\) based on the Raman-Compton approximation (Eq. (2.114)) and the Wentzel model (Eq. (2.145)), and the factorization of \(S(K, K', \Delta E)\) reduces to the factorization of \(F(\theta - \theta')\):

\[
F(\theta - \theta') = \frac{Z\theta_A^2}{\theta_A^2 + (\theta - \theta')^2},
\]

(D.1)

We define \(\nu = \theta/\theta_A\) and temporarily leave \(Z\) out, Eq. (D.1) becomes

\[
F(\nu - \nu') = \frac{1}{1 + (\nu - \nu')^2}.
\]

(D.2)

In order to approximate \(F\) in the form of \(F' = \sum_m \tilde{g}_m(\nu)\tilde{g}_m(\nu')\), where \(\tilde{g}_m(\nu)\) and \(\tilde{g}_m(\nu')\) are the functions of \(\nu\) and \(\nu'\), respectively, we make the Ansatz

\[
F' = \frac{a\nu \nu' + b\nu + c}{(1 + d\nu^2)(1 + d\nu'^2)},
\]

(D.3)

where \(a\), \(b\), \(c\) and \(d\) are coefficients. In order to compare Eqs. (D.2) and (D.3), we can discuss two cases - When \(\nu \neq \nu'\), the order of \(F\) is \(-2\), and so is the order of \(F'\); when \(\nu = \nu'\), \(F\) is a constant, however the order of \(F'\) is still \(-2\). Both \(\nu\) and \(\nu'\) are 2-dimensional vectors, and there are infinite positional relations between the two vectors. The relation \(\nu = \nu'\) represents only a special case. We can try to choose proper parameters of \(a\), \(b\), \(c\) and \(d\), in order to minimize the influence of the unbalanced order caused by this special case.

Assuming the angle between the two vectors \(\nu\) and \(\nu'\) is \(\alpha\) (\(0 \leq \alpha < 2\pi\)), we can write \(F\) and \(F'\) separately as

\[
F = \frac{1}{1 + \nu^2 + \nu'^2 - 2\nu\nu' \cos \alpha}.
\]

(D.4)

\(^{1}\)This chapter is adapted based on 75.
APPENDIX D. THE FACTORIZATION OF THE MDFF

and

\[ F' = AX \]
\[ = \begin{pmatrix} \frac{uv'}{(1 + dv^2)(1 + dv'^2)} & \frac{uv' \cos \alpha}{(1 + dv^2)(1 + dv'^2)} & \frac{1}{(1 + dv^2)(1 + dv'^2)} \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}. \] (D.5)

Our problem becomes to minimize the absolute difference \(|AX - F|\). We apply least-square method in terms of matrix. If there are \(I, J\) and \(K\) possible values for \(v, v'\) and \(\alpha\), respectively, then \(A\) is a matrix with \(I \times J \times K\)-dimensional column space. Similarly, \(F\) is a column vector with \(I \times J \times K\) dimensions. In order to minimize the distance \(|F - AX|\), \(AX\) needs to be the projection of \(F\) onto the column space of \(A\). Under this condition, \(A\) should be perpendicular to \(F - AX\), which leads to

\[ A^T (F - AX) = 0 \] (D.6)

or

\[ X = (A^T A)^{-1} A^T F. \] (D.7)

\(A^T A\) and \(A^T F\) can be calculated separately as

\[ A^T A = \begin{pmatrix} \sum_{i=1}^{I} \sum_{j=1}^{J} \sum_{k=1}^{K} \frac{(v_i v'_j)^2}{(1 + dv^2)(1 + dv'^2)} & \sum_{i=1}^{I} \sum_{j=1}^{J} \sum_{k=1}^{K} \frac{v_i v'_j \cos \alpha_k}{(1 + dv^2)(1 + dv'^2)} & \sum_{i=1}^{I} \sum_{j=1}^{J} \sum_{k=1}^{K} \frac{1}{(1 + dv^2)(1 + dv'^2)} \\ \sum_{i=1}^{I} \sum_{j=1}^{J} \sum_{k=1}^{K} \frac{(v_i v'_j)^2 \cos \alpha_k}{(1 + dv^2)(1 + dv'^2)} & \sum_{i=1}^{I} \sum_{j=1}^{J} \sum_{k=1}^{K} \frac{(v_i v'_j \cos \alpha_k)^2}{(1 + dv^2)(1 + dv'^2)} & \sum_{i=1}^{I} \sum_{j=1}^{J} \sum_{k=1}^{K} \frac{v_i v'_j \cos \alpha_k}{(1 + dv^2)(1 + dv'^2)} \\ \sum_{i=1}^{I} \sum_{j=1}^{J} \sum_{k=1}^{K} \frac{v_i v'_j}{(1 + dv^2)(1 + dv'^2)} & \sum_{i=1}^{I} \sum_{j=1}^{J} \sum_{k=1}^{K} \frac{v_i v'_j \cos \alpha_k}{(1 + dv^2)(1 + dv'^2)} & \sum_{i=1}^{I} \sum_{j=1}^{J} \sum_{k=1}^{K} \frac{1}{(1 + dv^2)(1 + dv'^2)} \end{pmatrix} \] (D.8)

and

\[ A^T F = \begin{pmatrix} \sum_{i=1}^{I} \sum_{j=1}^{J} \sum_{k=1}^{K} \frac{v_i v'_j}{(1 + dv^2)(1 + dv'^2)(1 + v_i^2 + v_j^2 - 2 v_i v'_j \cos \alpha_k)} \\ \sum_{i=1}^{I} \sum_{j=1}^{J} \sum_{k=1}^{K} \frac{v_i v'_j \cos \alpha_k}{(1 + dv^2)(1 + dv'^2)(1 + v_i^2 + v_j^2 - 2 v_i v'_j \cos \alpha_k)} \\ \sum_{i=1}^{I} \sum_{j=1}^{J} \sum_{k=1}^{K} \frac{1}{(1 + dv^2)(1 + dv'^2)(1 + v_i^2 + v_j^2 - 2 v_i v'_j \cos \alpha_k)} \end{pmatrix}. \] (D.9)

If the number of the sampling points \(K\) is large enough, the term contains \(\cos \alpha\) in the matrix \(A^T A\) should result in 0; since the integral of \(\cos \alpha\) in the space \(0 \leq \alpha \leq 2\pi\) is 0.

The variables \(v\) and \(v'\) are in the same range. \(v\) is the function of \(\theta\) and \(\theta_A\), namely

\[ v = \frac{\theta}{\theta_A} = \frac{q/k}{q_A/k} = \frac{q}{1/(a_H Z^{-1/3})} = a_H Z^{-1/3} q, \] (D.10)

where the Bohr radius \(a_H = 0.529\) Å. We can approximate the value of \(v\) by taking silicon as an example (\(Z = 14\)). The maximum \(q\) cannot exceed the instrumental resolution. For the \textbf{SALVE II} microscope operated at 20 kV, the instrumental resolution is worse than 1 Å. In this case, \(v\) is around 0.22. One can safely assume \(0 \leq v \leq 0.5\). The
variable $\nu'$ is defined in the same range of values as $\nu$.

The accuracy of the approximation can be evaluated based on the correlation coefficient $R(F, F')$ and the variance $Var(|F - F'|)$. Tab. D.1 showing the calculated $a$, $b$, and $c$ for different $d$ values in Eq. (D.3), as well as the corresponding $R(F, F')$ and $Var(|F - F'|)$.

Based on the correlation and variance analysis, the case corresponding to $d = 1$ leads to the maximum correlation between the original function $F$ and the approximation $F'$. The correlation analysis for the case of $d = 1$ with respect to the angle $\alpha$ shows that the worst correlation corresponds to the case $\alpha = 0$, where $\nu$ and $\nu'$ lie parallel. Following Eq. (D.3) we have already discussed about the problem of unbalanced order between the approximation and the original function in the case of $\nu = \nu'$, which is included in the case $\alpha = 0$. We expect that the influence of the unbalanced order can be roughly compensated by properly choosing a parameter $d$. Fig. D.1 shows the plots of original function $F$, approximation function $F'$ and the difference $F' - F$ in the case of $\nu = \nu'$. In this case the correlation coefficient between the approximation $F'$ and the original function $F$ is 0.9823; the mean value and the variance of $|F - F'|$ are $E(|F - F'|) = 9.6 \times 10^{-3}$ and $Var(|F - F'|) = 7.365 \times 10^{-5}$, respectively. Since $R(F, F')$
is close to 1, and the mean value $E(|F - F'|)$ as well as the variance $Var(|F - F'|)$ is much smaller than 1, we confirm

$$F' = \frac{0.32\nu\nu' + 1.64\nu\nu' + 1}{(1 + \nu^2)(1 + \nu'^2)}$$

(D.11)

is a good approximation for Eq. (D.2). Substituting $\nu = \theta/\theta_A$ back to Eq. (D.11) and multiplying the factor $Z$, we obtain

$$F(\theta - \theta') \approx Z \frac{0.32\theta^2\theta' + 1.64\theta^2\theta' + \theta^4}{(\theta^2_A + \theta^2)(\theta^2_A + \theta'^2)}.$$  

(D.12)

Figure D.1: Function $F$ and its approximation $F'$ for $\alpha = 0$. The correlation coefficient between the approximation and the original function is 0.9823 in this case, and the variance $Var(|F - F'|)$ equals $7.365 \times 10^{-5}$. Reproduced from Ultramicroscopy with the reference [75].
Appendix E

The fitting of the MTFs for the SALVE II microscope

The MTF data (Fig. E.1) for the SALVE microscope at 20 kV, 40 kV, 60 kV and 80 kV were measured utilizing the method of averaged single electron events detected by the T416 camera [116,117].

The measured MTF (Fig. E.1) are fitted by Eq. (E.1) and the coefficients are listed in Tab. E.1. $R^2$ is the coefficient of determination, which shows the correlation between the original MTF profile and the fitted function. Large $R^2$ indicates good fitting.

\[
MTF(q) = \frac{a_1 - a_2}{1 + \left(\frac{q}{2a_3 q_N}\right)^{a_4}} + a_2
\]  

(E.1)

$a_1, a_2, a_3$ and $a_4$ are the coefficients to be determined. $q_N$ is the Nyquist frequency related to the sampling $\delta$ by $\delta = 1/(2q_N)$. Usually the x-axis of the MTF profile represents the frequency corresponding to a certain feature sampled with $n$ pixels in real space, and $1/n$ has the unit of pixel$^{-1}$. Here we have used another notation in order to facilitate the image calculation. By multiplying both the numerator and denominator with the sampling $\delta$, we obtain

\[
\frac{1}{n} = \frac{\delta}{n\delta} = \frac{1/n\delta}{1/\delta}.
\]

(E.2)

The denominator is the reciprocal of the sampling $\delta$, which equals the maximum sampling frequency or two times of the Nyquist frequency $q_N$. The numerator represents the spatial frequency $q$ corresponding to the feature sampled with $n$ pixels in real space. We obtain

\[
\frac{1}{n} = q\delta = \frac{q}{2q_N}
\]

(E.3)

This chapter is adapted based on [77].
Table E.1: The fitting coefficients of $a_1$, $a_2$, $a_3$ and $a_4$ for Eq. (E.1). Reproduced from Ultramicroscopy with the reference [77].

<table>
<thead>
<tr>
<th>HT (kV)</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$a_4$</th>
<th>$R^2$</th>
</tr>
</thead>
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<tr>
<td>20</td>
<td>99.97</td>
<td>-6.71</td>
<td>0.27</td>
<td>2.19</td>
<td>0.99972</td>
</tr>
<tr>
<td>40</td>
<td>98.75</td>
<td>-2.87</td>
<td>0.24</td>
<td>2.55</td>
<td>0.99971</td>
</tr>
<tr>
<td>60</td>
<td>98.83</td>
<td>-3.14</td>
<td>0.25</td>
<td>2.53</td>
<td>0.99973</td>
</tr>
<tr>
<td>80</td>
<td>98.48</td>
<td>-2.52</td>
<td>0.24</td>
<td>2.63</td>
<td>0.99965</td>
</tr>
</tbody>
</table>

Figure E.1: Experimentally measured MTFs for the SALVE II microscope at 20 kV, 40 kV, 60 kV and 80 kV. At Nyquist frequency where $q/(2q_N) = 0.5$, the MTF is between 0.1 and 0.15, indicating that the image contrast corresponding to this frequency has a loss of 85-90%. Reproduced from Ultramicroscopy with the reference [77].
Appendix F

Determination of the factor $\kappa$ in Eq. (8.6)\textsuperscript{1}

In order to show the correlation between the images calculated with finite electron doses and the ones calculated with infinite electron dose, we calculated the coefficient of determination $R^2$ (Fig. F.1). If we define

\begin{align*}
S_{12} &= \sum_{j=1}^{J} [\text{Pois}(D\delta^2 I_j) - \text{Pois}(D\delta^2 I_j)][I_j - \bar{I}], \quad (F.1) \\
S_{11} &= \sum_{j=1}^{J} [\text{Pois}(D\delta^2 I_j) - \text{Pois}(D\delta^2 I_j)]^2, \quad (F.2) \\
S_{22} &= \sum_{j=1}^{J} [I_j - \bar{I}]^2, \quad (F.3)
\end{align*}

then the coefficient of determination is expressed as

$$R^2 = \frac{S_{12}^2}{S_{11}S_{22}}. \quad (F.4)$$

The coefficient $R^2$ lies in the range of $[0, 1]$, where the number 1 indicates a perfect match and 0 indicates no match at all. $R^2$ increases smoothly with respect to the electron dose. When $R^2=1$, the atom contrast equals the value obtained with infinite dose $C_d = C_W = (I_b - I_a)/I_b$; and when $R^2=0$, the atom contrast $C_d$ is also 0. Therefore we can define the dose-dependent contrast by scaling $R^2$ with the contrast $C_W$ (Eq. (6.1)), resulting in Fig. F.2. One can see that for coarse sampling, the maximum atom contrast is smaller than for the case of fine sampling.

This trend is consistent with the evolution of atom contrast as a dependence on the electron dose (Fig. 8.1), and we can use Eq. (8.6) to fit the curves in Fig. F.2 shown as follows:

$$R^2 | \frac{I_b - I_a}{I_b} | = (\frac{\sigma(N)}{N\sigma(I)})^{-\kappa} | \frac{I_b - I_a}{I_b} | \quad (F.5)$$

\textsuperscript{1}This chapter is adapted based on \cite{77}.
results in
\[
\ln \frac{1}{R^2} = \kappa \ln \frac{\sigma(N)}{N \sigma(I)}.
\] (F.6)

Here all the terms in the logarithms are larger than 0. By linear fitting of \(\ln[\sigma(N)/(\bar{N} \sigma(I))]\) and \(\ln(1/R^2)\), we can obtain the coefficient \(\kappa\) which is the slope of the line. The fitting is displayed in Fig. F.3, where all the lines show similar slope.

The corresponding values of \(\kappa\) for different samplings obtained through linear fitting in Fig. F.3 are listed in Tab. F.1. Since the results are very close, we can assume \(\kappa=2\) for all samplings.

Table F.1: The fitting coefficients of \(\kappa\) for Eq. (F.6). Reproduced from Ultramicroscopy with the reference 77.

<table>
<thead>
<tr>
<th>sampling (Å/pixel)</th>
<th>(\kappa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>1.981</td>
</tr>
<tr>
<td>0.3</td>
<td>1.987</td>
</tr>
<tr>
<td>0.15</td>
<td>1.998</td>
</tr>
<tr>
<td>0.075</td>
<td>2.003</td>
</tr>
<tr>
<td>0.038</td>
<td>2.013</td>
</tr>
<tr>
<td>0.019</td>
<td>2.006</td>
</tr>
<tr>
<td>0.01</td>
<td>2.000</td>
</tr>
</tbody>
</table>

This result \(\kappa = 2\) for all samplings is not surprising. In the case of high dose, \(\text{Pois}(D \delta^2 I_j) \approx D \delta^2 I_j\) and \(\text{Pois}(D \delta^2 I_j) \approx D \delta^2 \bar{I}\). Therefore

\[
S_{12} = \sum_{j=1}^{J} [\text{Pois}(D \delta^2 I_j) - \text{Pois}(D \delta^2 I_j)] [I_j - \bar{I}]
\approx D \delta^2 \sum_{j=1}^{J} [I_j - \bar{I}]^2 = D \delta^2 S_{22},
\] (F.7)

\[
R^2 = \frac{S_{12}^2}{S_{11} S_{22}} \approx \frac{(D \delta^2)^2 \sum_{j=1}^{J} [I_j - \bar{I}]^2}{\sum_{j=1}^{J} [\text{Pois}(D \delta^2 I_j) - \text{Pois}(D \delta^2 I_j)]^2}
= \left( \frac{D \delta^2 \sigma(I)}{\sigma(N)} \right)^2 \approx \left( \frac{D \delta^2 \bar{I} \sigma(I)}{\sigma(N)} \right)^2 = \left( \frac{\bar{N} \sigma(I)}{\sigma(N)} \right)^2.
\] (F.8)

The relation between \(R\) and \(\bar{N} \sigma(I)/\sigma(N)\) is then clarified. Here the relation \(\bar{I} \approx 1\) has been used.
Figure F.1: The coefficient of determination $R^2$ shows the correlation between the images calculated with finite and infinite electron doses at different samplings for 80 kV. Reproduced from Ultramicroscopy with the reference [77].

Figure F.2: The atom contrast obtained at 80 kV by scaling the coefficient $R^2$ with the contrast obtained for infinite dose, namely $R^2|\frac{I_b - I_a}{I_b}|$. The maximum atom contrast is lower for coarse sampling than for fine sampling. Reproduced from Ultramicroscopy with the reference [77].
Figure F.3: The linear fitting of $\ln\left[\sigma(N)/(\bar{N}\sigma(I))\right]$ and $\ln(1/R^2)$. The slope of the line is the coefficient $\kappa$ and the slope is very close for different samplings. The calculation is performed for the accelerating voltage of 80 kV. Reproduced from Ultramicroscopy with the reference [77].
References


REFERENCES


REFERENCES


[73] H. Rose, “Elastische und unelastische Streuung.”.
REFERENCES


Acknowledgement

Writing a thesis is absolutely an effective way to lose weight. All the struggles over the texts, formulas and calculations finally result in the death of thousands of lipocytes. At the end of the long battle against my weight, which I did not even intend, I have some words to say.

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VERÖFFENTLICHUNGEN


Erklärung

Ich versichere hiermit, daß ich die Arbeit selbständig angefertigt habe und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt sowie die wörtlich oder inhaltlich übernommenen Stellen als solche kenntlich gemacht habe.

Ulm, den 28.02.2014

Zhongbo Lee