# Forward and inverse problems in x-ray fluorescence holography

by

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# Oświadczenie

Ja niżej podpisany Dawid Tadeusz Dul (nr indeksu: 1015525 463) doktorant Wydziału Fizyki, Astronomii i Informatyki Stosowanej Uniwersytetu Jagiellońskiego oświadczam, że przedłożona przeze mnie rozprawa doktorska pt. Forward and inverse problems in x-ray fluorescence holography jest oryginalna i przedstawia wyniki badań wykonanych przeze mnie osobiście, pod kierunkiem dr hab. Pawła Koreckiego. Pracę napisałem samodzielnie.

Oświadczam, że moja rozprawa doktorska została opracowana zgodnie z Ustawą o prawie autorskim i prawach pokrewnych z dnia 4 lutego 1994 r. (Dziennik Ustaw 1994 nr 24 poz. 83 wraz z późniejszymi zmianami).

Jestem świadom, że niezgodność niniejszego oświadczenia z prawdą ujawniona w dowolnym czasie, niezależnie od skutków prawnych wynikających z ww. ustawy, może spowodować unieważnienie stopnia nabytego na podstawie tej rozprawy.

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 $podpis \ doktoranta$ 

### Abstract

When attempting to describe a typical experiment in physics one usually considers two situations. Either one is given the initial conditions/parameters of the experiment and one attempts to model the outcome or one is given the outcome and wishes to determine the initial conditions/parameters. The first situation is often referred to as the forward problem while the second one as the inverse problem. These problems are typical for methods of atomic structure determination. The initial conditions and parameters in such experiments are given by the sample's structure, detection geometry, source and properties of the used radiation as well as other factors. The outcome can be, for example, a diffraction pattern.

In this work, we consider forward and inverse problems in x-ray fluorescence holography (XFH), an atomic structure imaging technique that gives access to both the amplitude and phase of the x-ray radiation scattered from the sample. It is a versatile tool that can be used to obtain three dimensional atomic images of long range order as well as local atomic structure around specifically chosen elements inside crystals.

In the first part of this work we discuss white beam XFH. We improve the description of white beam holograms by approximating the effective x-ray spectra with the Gumbel distribution. We then concentrate on structure retrieval and give a quantitative description of the continuous spherical wavelet transform as applied to white beam XFH. This is accomplished by deriving analytic formulas for the radial and angular resolution as well as explicitly demonstrating that the wavelet approach is sensitive to local atomic arrangements. We propose a wavelet based reliability factor (R-factor) analysis which enables the location of impurities in the crystal lattice that occupy multiple sites.

The second part is dedicated to the study of matrix effects, i.e., beam attenuation and indirect excitation in XFH. By combining the theory of XFH with the methods of x-ray fluorescence spectroscopy we develop a model which takes matrix effect into account in XFH. We argue that in the presence of matrix effects element sensitivity of the measured holograms might be lost. It is shown that the loss of element sensitivity can lead to distortions and/or spurious maxima in the reconstruction. These can hinder atomic structure studies with XFH. As a solution to these problems we propose a correction procedure for matrix effects in both the monochromatic and white beam versions of XFH. The correction procedure allows one to restore element sensitivity of the measured holograms and opens way for quantitative structure analysis with XFH.

#### Streszczenie

Opis eksperymentów w fizyce można zwykle sprowadzić do dwóch rodzajów zagadnień. Pierwsze z nich to tzw. problem bezpośredni, w którym staramy się modelować/przewidzieć wynik eksperymentu mając do dyspozycji warunki początkowe. Drugie zagadnienie to tzw. problem odwrotny, w którym mamy do dyspozycji wynik eksperymentu i staramy się odtworzyć warunki początkowe. Te dwa zagadnienia są powszechne dla eksperymentów, których celem jest wyznaczenie struktury atomowej. Warunki początkowe w tego typu eksperymentach są zadane przez strukturę próbki, geometrię eksperymentu, źródło promieniowania oraz inne czynniki. Wynikiem tego typu eksperymentów mogą być np. obrazy dyfrakcyjne.

W niniejszej pracy rozważamy problemy bezpośrednie i odwrotne w fluorescencyjnej holografii rentgenowskiej (FHR). Jest to metoda obrazowania struktury atomowej, która zapewnia dostęp zarówno do amplitudy, jak i fazy promieniowania rentgenowskiego rozproszonego na próbce. Fluorescencyjna holografia rentgenowska jest uniwersalnym narzędziem, które pozwala obrazować, w trzech wymiarach, daleko zasięgową strukturę atomową jak i lokalne otoczenie wybranych pierwiastków w kryształach.

Pierwsza część pracy dotyczy tzw. "białej" FHR. Ulepszamy w niej opis białych hologramów rentgenowskich poprzez przybliżenie efektywnych widm rentgenowskich rozkładem Gumbela. Następnie koncentrujemy się na rekonstrukcji struktury atomowej z białych hologramów przy pomocy ciągłej transformaty falkowej na sferze. Podajemy ilościowy opis tej metody wyprowadzając wzory na rozdzielczość a także bezpośrednio pokazująć iż metoda ta jest czuła na lokalną strukturę atomową. Następnie przedstawiamy metodę analizy białych hologramów rentgenowskich, opartą o analizę falkową, pozwalającą obrazować domieszki w kryształach, które obsadzają kilka pozycji atomowych równocześnie.

Druga część pracy poświęcona jest efektom absorpcji wiązki oraz wtórnej fluorescencji w FHR. Łącząc metody spektroskopii rentgenowskiej i FHR budujemy model, który bierze te efekty pod uwagę i pozwala je opisać. Argumentujemy, że w obecności tych efektów czułość chemiczna, jedna z podstawowych własności zarówno monochromatycznych jak i białych hologramów rentgenowskich, może zostać stracona. To z kolei może prowadzić do dystorsji i artefaktów w rekonstrukcjach tych hologramów co z kolei utrudnia badania przy użyciu FHR. W pracy została zaproponowana procedura, która pozwala wyeliminować wpływ efektów absorpcji wiązki i wtórnej fluorescencji w monochromatycznej jaki i białej FHR. Procedura ta pozwala przywrócić czułość chemiczną hologramów i umożliwia ilościową analizę struktury atomowej przy użyciu FHR.

I would like to express my deep gratitude to my supervisor dr hab. Pawel Korecki for his support and encouragement during the past few years. I am extremely grateful for all the fruitful discussions, constructive remarks, insights and his optimism. I would also like to thank all the members of the Synchrotron Radiation Department of the Jagiellonian University for their help.

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# A WORD OF INTRODUCTION

Knowledge about atomic structure lies at the heart of understanding some of the most remarkable properties of materials. If one takes a look at the amount of structures that have been resolved so far then the number is overwhelming. The Crystallography Open Database and the Worldwide Protein Data Bank together contain more than four hundred thousand entries (Jones 2014). Among them one can find structures of metals, minerals, small biological molecules, proteins and other organic structures. Every day new structures are being added to these databases providing invaluable information for basic research and technical application. Most of this information was and still is being obtained by means of diffractive methods.

Owing to the enormous success of diffractive methods one might be tempted to say that nowadays, atomic structure determination is an easy task. Making such a statement, however, would be certainly an exaggeration. In a standard diffractive experiment one illuminates a sample with, e.g., x-rays and measures the intensity of the elastically scattered radiation. However, to unambiguously determine the atomic structure one needs the intensity as well as the phase of the scattered radiation. The lack of phase information in diffractive measurements and the problems that arise because of that are known in crystallography as the *phase problem* (Taylor 2003). The phase problem has been extensively investigated and a number of approaches for phase retrieval have been developed. Among them are the purely computational approaches like the Patterson function or direct methods and experimental ones like the multi-wavelength anomalous diffraction and multiple isomorphous replacement (Shen et al. March 2006). Despite, all these advancements phase retrieval is not always straightforward and, in some cases, not possible at all. The desire for a direct solution of the phase problem, i.e., a technique which would directly give access to the phase of the scattered radiation was the main driving force behind the development of x-ray fluorescence holography (XFH) - the topic of this work.

X-ray fluorescence holography was first proposed by Szöke (1986) and based on Denis Gabor's original idea of holography (Gabor 1948). The experimental realization of the technique came after feasibility studies (Tegze & Faigel 1991, Len et al. 1994) in the mid 90s of the past century (Tegze & Faigel 1996, Gog et al. 1996). X-ray fluorescence holography combines x-ray diffraction and x-ray fluorescence spectroscopy and, as every holographic technique, provides access to both the amplitude and phase of the scattered radiation. From the point of view of structure determination XFH can be considered as a versatile technique. It can be used to obtain the long range order component of the electron density and to image local atomic arrangements in three dimensions. It

is especially suitable for the location of atoms, e.g., dopants in the crystal lattice and the determination of the local atomic structure around them. A review on the early days of XFH can be found in Faigel et al. (2007). Currently, XFH is being used for atomic structure studies on regular basis (Hayashi et al. 2012, 2014).

When describing an experiment in physics one is usually interested in solving two general problems (Tarantola 2004). In the first of these, known as forward or direct problem, one is given the initial experimental conditions and one attempts to describe/predict the result of the experiment. In the second problem, known as the inverse problem, one is given the results of the experiment and one attempts to recreate the initial conditions. For example, in a typical diffraction experiment the initial conditions are given by the sample's structure, the experimental geometry and the type of radiation that is used. The result of such an experiment is a diffraction pattern from which one attempts to reconstruct the structure of the sample.

These two types of problems have been also heavily considered in XFH. On the one hand, a lot of effort has been put into the description of x-ray fluorescence holograms. This included classical (Adams et al. 1998, Tegze & Faigel 2001) and quantum (Fonda 1997, Nishino & Materlik 1999) electrodynamic calculations as well as the inclusion of various effects, i.e., incident-radiation polarization (Len et al. 1997), near field (Bai 2003) and extinction (Korecki, Novikov, Tolkiehn & Materlik 2004) effects. On the other hand, enormous effort has been put into structure reconstruction from x-ray fluorescence holograms. The early approach was made by Barton (1988, 1991), followed by Marchesini et al. (2002), Marchesini & Fadley (2003), Chukhovskii & Poliakov (2003), Nishino et al. (2002), Matsushita et al. (2005) and quite recently by Wang et al. (2012). Despite all these advancements there are still areas where improvement is possible and issues which, to the best knowledge of the author, have not been addressed.

One of the areas where improvement is possible is white beam XFH (Korecki et al. 2011) a variant of XFH where a polychromatic beam is used instead of a monochromatic one. In the description of white beam holograms it is important to accurately describe the shape of the incident x-ray spectra. These usually have the shape of a heavily skewed distribution but are currently being approximated by the Lorentz distribution which has an undefined skewness and is perfectly symmetric with respect to its center. Concerning the reconstruction of atomic structure from white beam holograms there are currently two methods: the approach based on the continuous spherical wavelet transform (Korecki, Novikov & Tolkiehn 2009) and the tomographic algorithm (Korecki et al. 2006*b*,*a*). The tomographic approach is only sensitive to long range order and its application usually requires some *a priori* knowledge about the crystal structure, e.g., the shape of the unit cell or the whole space group. The continuous spherical wavelet transform, on the other hand, is a model free approach, i.e., it does not require any *a priori* information and at the same time provides local structure information. However, it lacks quantitative description.

A different area that, to the author's best knowledge, has not been explored at all in XFH are the

so called matrix effects, i.e., beam attenuation (BA) and indirect excitation (IE). In a typical XFH experimental setup one illuminates the sample with an x-ray beam and measures x-ray fluorescence as a function of the sample-beam orientation. In such measurements, according to the methods of x-ray fluorescence spectroscopy, it is important to take into account the attenuation of the beam inside the sample. It is also important to account for indirect (secondary) excitation processes, i.e., processes in which atoms inside the sample are excited not by the x-ray beam but by the x-ray fluorescence from other atoms.

In this work we attempt to improve the description of white beam holograms and their structure reconstruction. We also tackle the problem of matrix effects in XFH. The original results presented in this work are based on three articles which were published in peer-reviewed journals, namely:

- Dul, D. T. & Korecki, P. (2012), 'Wavelet analysis of white beam x-ray fluorescence holograms: determination of lattice sites and imaging of local atomic structure', New Journal of Physics 14, 113044;
- Dul, D. T., Dąbrowski, K. M., & Korecki, P. (2013), 'Correction for beam attenuation and indirect extitation in x-ray fluorescence holography', EPL (Europhysics Letters) 104, 66001; and
- Dul, D. T., & Korecki, P. (2015), 'Matrix effects in white beam x-ray fluorescence holography', Journal of Applied Crystallography 48, 542.

Certain extensions and applications of the results presented in the thesis can be found in:

- Dąbrowski, K. M., & Dul, D. T., Roszczynialski, T. P., Korecki, P. (2013), 'Element sensitive holographic imaging of atomic structures using white x-rays', Physical Review B 87, 064111; and
- Dul, D. T., & Korecki, P. (2015) 'Matrix effects in x-ray fluorescence holography: samples of arbitrary thickness', Zeitschrift für Physikalische Chemie, in press.

The presented work is organized into five chapters.

In Chapter 1 we introduce the reader to XFH. We describe the basic concepts behind the formation of x-ray fluorescence holograms and describe the measurement process. An overview of the hologram reconstruction procedures is given.

Chapter 2 is entirely devoted to white beam XFH. We extend the monochromatic formalism from the first chapter to white beam XFH. We improve the description of white beam holograms by proposing a Gumbel distribution based approximation of white x-ray spectra which very well matches their shape. We give a quantitative description of the continuous spherical wavelet transform as applied to white beam XFH. This is accomplished by deriving analytic formulas for the radial and angular resolution as well as explicitly demonstrating that this approach is sensitive to local

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atomic arrangements. We extend the capabilities of the spherical wavelet transform by proposing a wavelet based reliability factor (R-factor) analysis which enables full three dimensional localization of impurities that occupy multiple sites. This wavelet based reliability factor analysis is based on the inverse windowed wavelet transform for which we derive a compact formula which allows its fast calculation in a single step.

In Chapters 3 and 4 we consider matrix effects in both monochromatic and white beam XFH. We base our considerations on the methods of x-ray fluorescence spectroscopy and develop a model which takes these effects into account. We show that in the presence of beam attenuation and indirect excitation the measured holograms cannot be regarded as element sensitive. On the contrary, a sort of "hologram mixing" takes place and a hologram measured for a given element should be rather regarded as a sum of holograms with appropriate coefficients. This kind of sum should involve holograms for all elements that constitute the sample. As a result, the amplitude of the holographic signal is reduced and its shape may change. This in turn may lead to distortions, abberations and/or spurious maxima in the reconstruction. For monochromatic XFH we propose a correction procedure which allows to correct for matrix effects and verify it on experimental data. In the case of white beam XFH we propose a correction procedure that is valid for hard x-ray spectra that have a lower cut off far above the K edges of the elements that constitute the sample. Our considerations free XFH from the burden of matrix effects and open way for proper atomic structure analysis.

In Chapter 5 we summarize our main results.

#### CHAPTER 1

# X-RAY FLUORESCENCE HOLOGRAPHY (XFH)

#### 1.1 The internal source/detector concept

Our journey with XFH begins with Denis Gabor's original microscopic principle (Gabor 1948) which is presented in figure 1.1(a). A primary wave is focused and, as it diverges, is elastically scattered by an object that is placed downstream the focus. The interference pattern of the two waves, also known as the hologram, is recorded by a detector placed in the far field. The primary wave is referred to as the *reference wave* while the scattered wave is referred to as the *object wave*. The primary wave is assumed to be monochromatic and much stronger then the scattered wave. We write the amplitude of the reference wave as  $R = R_0 e^{i\phi_R}$  and the amplitude of the object wave as  $O = O_0 e^{i\phi_O}$ . The intensity I at the detector is proportional to the absolute value

$$I \propto |R+O|^2 = |R_0|^2 + 2R_0O_0\cos(\phi_R - \phi_O) + |O_0|^2$$
(1.1)

which is the basic equation of holography (Gabor 1949). Apart from the terms proportional to the intensity of the reference wave  $(|R_0|^2)$  and object wave  $(|O_0|^2)$  it also contains an interference part  $[2R_0O_0\cos(\phi_R - \phi_O)]$ . The object part  $|O_0|^2$  is negligible, since it is assumed that  $|R_0|^2 \gg |O_0|^2$ . The presence of the interference component enables the determination of phase, and thus, a three dimensional reconstruction of the object.

X-ray fluorescence holography in the normal, also referred to as the emission, mode was proposed by Szöke (1986) and realized by Tegze & Faigel (1996). It is an almost direct realization of Gabor's scheme in the case of atomic systems. Consider a system of two atoms as in figure 1.1(b). The system is irradiated by a beam of monochromatic x-rays. The energy of the beam is assumed to be higher then the K edge (other edges are also possible) of atom A. As a result atom A will absorb the incoming excitation x-rays and remit fluorescence x-rays (e.g., K $\alpha$  radiation). Atom A replaces the focus in the original Gabor's scheme. It can be considered as an internal source of x-ray radiation, internal in the sens that it is part of the considered atomic system. The emitted fluorescence x-rays will elastically scatter from atom B. The detector in the far field records the interference pattern, a hologram, which results from a superposition of the scattered (object wave) and unscattered (reference wave) fluorescence x-rays. Both the emitted and scattered fluorescence x-rays propagate in all directions. Thus, to measure the whole hologram the detector usually moves on a surface of a sphere which is centered at the position of the internal source. If atom A has more neighbors then just the atom B then each neighbor will scatter the emitted x-ray fluorescence and



Figure 1.1: Gabor's holography and the two modes of XFH. The figure is analogous to Figure 1 in Len, Gog, Fadley & Materlik (1997). (a) Original Gabor's holographic setup (Gabor 1948). A beam of radiation is focused and as it diverges it is scattered from an object. The superposition of the diverging wave (reference wave) and the scattered wave (object wave) is recorded by a flat detector. (b) The normal mode of x-ray fluorescence holography (Szöke 1986, Tegze & Faigel 1996). The role of the focus, in Gabor's original setup, is now played by atom A which emits fluorescence x-rays. It is being excited by the incoming x-ray beam and becomes an internal source of x-rays. The emitted fluorescence x-rays are scattered of a neighboring atom B. The resulting hologram is recorded by a detector in the far field which moves on the surface of the sphere. (c) The inverse mode of x-ray fluorescence holography (Gog et al. 1996). It is the time reversed version of the normal mode. The system of atoms is illuminated by a coherent x-ray wave. The wave reaches atom A directly or indirectly after being scattered from atom B. The resulting hologram is probed by atom A which works as an internal detector. It is indirectly measured through x-ray fluorescence by an external detector.

contribute its own scattered wave to the resulting hologram. A system of atoms might also contain more then one internal source. In such a case each of the internal sources will produce a hologram of its own and a hologram averaged over all the sources will be recorded.

By means of the reciprocity in optics (Potton 2004) x-ray fluorescence holography can be realized in a different way. In the inverse mode of XFH (Gog et al. 1996), sometimes also referred to as the absorption mode, the position of the x-ray source and the detector are interchanged. The directions of all the optical paths are reversed. Consider the situation in figure 1.1(c). The system of two atoms is irradiated by a coherent x-ray beam. This beam can reach atom A directly or after being scattered from its neighbor. The unscattered part of the x-ray beam is the reference wave whereas the scattered part is the object wave. As the direction of the beam, given by the wave vector  $\mathbf{k_x}$ , changes so does the path difference between the reference and object waves. The superposition of the two waves produces a hologram which is probed at the position of atom A. Here, atom A works as an internal detector. The intensity of the x-ray field at its position is proportional to the amount of x-ray fluorescence that it emits. The actual detector that measures the emitted fluorescence x-rays is outside the atomic system. One can say that the fluorescence photons convey the information about the hologram from the internal detector to the actual detector.

For completeness it must be mentioned that the ideas presented in figures 1.1(b) and 1.1(c) are much broader and can be also realized with other types of radiation, e.g., electrons,  $\gamma$ -rays or even neutrons. Each of these has its own advantages and disadvantages and can be applied to solve a specific problem. For example instead of using fluorescence x-rays one can use photoelectrons or Auger electrons (Harp et al. 1990, Thevuthasan et al. 1993, Li et al. 1993). This is sometimes desired since due to the short mean free path of electrons they are sensitive only to the surface of the sample. A comparative study of photoelectron holography and XFH was performed by Len et al. (1994). A different, interesting approach, known as bremsstrahlung x-ray holography, combines an incident electron beam with bremsstrahlung photons that are produced inside the sample (Bompadre et al. 1999). When it comes to imaging of light atoms, e.g., hydrogens, the usage of neutron beams instead of x-ray beams is desirable. Holography with thermal neutrons has been demonstrated in a number of experiments (Sur et al. 2001, Cser et al. 2002, 2006, Hayashi et al. 2015). Finally, the Mössbauer effect can be used to perform  $\gamma$ -ray holography (Korecki et al. 1997, 1999, 2001, 2004). Since this work focuses solely on x-rays we will not discuss these various types of imaging techniques any further.

We now attempt to quantify the description of XFH. We concentrate on the inverse mode with which we will deal in the reminder of the text. In our discussion we mainly follow the works of Adams et al. (1998) and Tegze & Faigel (2001).

Consider a system that is composed of an atom and a point scatterer (e.g., an electron) as in figure 1.2(a). The electron is placed at  $\mathbf{r}'$  and the detector atom is placed at  $\mathbf{R}_i$ . The *i* index denotes the type of the detector atom, e.g., i = Ga or i = Cu. The system is illuminated by a beam of x-rays

which is approximated with a plane wave. We attempt to calculate the x-ray wave field intensity at the position of the detector atom.



Figure 1.2: (a) A model absorbing atom - point scatterer system. (b) A model absorbing atom - scattering atom system. (c) An example x-ray fluorescence hologram for the absorbing atom - point scatterer system from (a) calculated with equation (1.9). (d) An x-ray fluorescence hologram calculated for a absorbing atom - gallium scattering atom system. The hologram was calculated with equation (1.10). In (c) and (d) the incident energy was set to 16.0 keV ( $k = 8.12 \text{ Å}^{-1}$ ) and  $\mathbf{r}' = \mathbf{r}'_{\ell} = (0, 0, 3.19 \text{ Å})$ . (e) A hologram for GaAs. The gallium atom was chosen as the detector atom (i = Ga). The hologram was generated with equation (1.10) for an atomic cluster that had a radius of 50 Å and E = 15.0 keV ( $k = 7.6 \text{ Å}^{-1}$ ).

The amplitude of the incident x-ray wave can be written as

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0 \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}},\tag{1.2}$$

where  $\mathbf{r}$  is the space coordinate,  $\mathbf{k} = -\mathbf{k_x}$  and  $\mathbf{k_x}$  is the wave vector of the incident plane wave. In other words,  $\mathbf{k}$  is antiparallel to the wave vector. The incident wave is elastically scattered from the electron. When interacting with the x-ray wave field, the electron can be treated as a dipole with a dipole moment equal to  $\mathbf{p} = -r_e \mathbf{E}_0 e^{-i\mathbf{k}\cdot\mathbf{r}'}/k^2$ , where  $r_e = 2.82 \times 10^{-5}$  Å is the Thomson scattering length and  $k = |\mathbf{k}|$ . The amplitude of the scattered wave at the position of the detector atom is

given by the standard dipole radiation formula (Jackson 1998)

$$\mathbf{E}_{s}(\mathbf{R}_{i},\mathbf{r}',\mathbf{k}) = k^{2} \left[ \hat{\mathbf{v}} \times (\mathbf{p} \times \hat{\mathbf{v}}) \right] \frac{\mathrm{e}^{\mathrm{i}k|\mathbf{R}_{i}-\mathbf{r}'|}}{|\mathbf{R}_{i}-\mathbf{r}'|},\tag{1.3}$$

where  $\hat{\mathbf{v}} = \mathbf{v}/|\mathbf{v}|$  and  $\mathbf{v} = \mathbf{R}_i - \mathbf{r}'$ . If the electron is replaced with an atom, as in figure 1.2(b), then the incoming x-ray wave will be scattered from all its electrons. At this point it is convenient to introduce the electron density  $\rho(\mathbf{r})$ . For systems of atoms the electron density can be represented as

$$\rho(\mathbf{r}) = \sum_{\ell} \rho_{\ell}(\mathbf{r} - \mathbf{r}_{\ell}'), \qquad (1.4)$$

where the  $\ell$  sum runs over all the atoms in the considered system (e.g., a crystal) and  $\mathbf{r}'_{\ell}$  denotes the position of each of the atoms. The total wave field at the position of the detector atom will be a sum of the incident plane wave and the waves scattered from the electron distribution, namely

$$\mathbf{E}_{i}(\mathbf{R}_{i},\mathbf{k}) = \mathbf{E}(\mathbf{R}_{i}) + \int \rho(\mathbf{r}) \mathbf{E}_{s}(\mathbf{R}_{i},\mathbf{r},\mathbf{k}) \mathrm{d}\mathbf{r}.$$
(1.5)

The number of fluorescence photons that the detector atom emits is proportional to the wave field intensity I at  $\mathbf{R}_i$ . This in turn is proportional to the square of  $\mathbf{E}_i$  and reads

$$|\mathbf{E}_{i}(\mathbf{R}_{i},\mathbf{k})|^{2} = \mathbf{E}_{0}^{2} - 2r_{e}\operatorname{Re}\left[\int \rho(\mathbf{r})\mathbf{E}(\mathbf{R}_{i})\cdot\mathbf{E}_{s}(\mathbf{R}_{i},\mathbf{r},\mathbf{k})\mathrm{d}\mathbf{r}\right] + O(r_{e}^{2}).$$
(1.6)

The term proportional to  $r_e^2$  is neglected. The final expression for the intensity is

$$I \propto |\mathbf{E}_i(\mathbf{R}_i, \mathbf{k})|^2 = \mathbf{E}_0^2 \left[1 + \chi_i(\mathbf{k})\right], \qquad (1.7)$$

where

$$\chi_i(\mathbf{k}) = -2r_{\rm e} \operatorname{Re}\left[\int P\rho(\mathbf{r}) \frac{\mathrm{e}^{\mathrm{i}k|\mathbf{R}_i - \mathbf{r}|}}{|\mathbf{R}_i - \mathbf{r}|} \mathrm{e}^{\mathrm{i}\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{r})} \mathrm{d}\mathbf{r}\right]$$
(1.8)

and

$$P = 1 - \frac{(\mathbf{E}_0 \cdot \hat{\mathbf{v}})^2}{\mathbf{E}_0^2}$$

The polarization factor P results from the dot product  $\mathbf{E}_0 \cdot ((\hat{\mathbf{v}} \times \mathbf{E}_0) \times \hat{\mathbf{v}}) = \mathbf{E}_0^2 - (\mathbf{E}_0 \cdot \hat{\mathbf{v}})^2$ . Equation (1.6) has the same form as (1.1). One can easily recognize terms in the two equations that correspond to one another. The  $\chi_i$  part can be interpreted as a hologram of the atomic structure around the detector atom.

One can obtain an interesting, special case of equation (1.8) for  $\rho(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}')$  which corresponds to a point scattering object placed at  $\mathbf{r}'$ . This was actually the starting point of our discussion. In this case (1.8) reduces to

$$\chi(\mathbf{k}) = -2r_{\mathrm{e}}\mathrm{Re}\left[\frac{\mathrm{e}^{\mathrm{i}[k|\mathbf{R}_{i}-\mathbf{r}'|+\mathbf{k}\cdot(\mathbf{R}_{i}-\mathbf{r}')]}}{|\mathbf{R}_{i}-\mathbf{r}'|}\right].$$
(1.9)

Without loss of generality to the results presented in this work we have neglected the polarization term in (1.9). Polarization effects have been studied in XFH by Len et al. (1997) and Bortolani et al. (2003). It is well established how they affect the holograms and their reconstruction.

With the help of equation (1.4) one can rewrite  $\chi_i$  as a convenient sum over the scattering atoms. To do so one assumes that the electron density of the scattering atom is highly localized around  $\mathbf{r}'_{\ell}$ . This is sometimes referred to as the plane wave approximation or the small atom approximation. This is a standard approximation in XFH but at the same time a rather crude one. Within it the scattered wave is effectively treated as a plane wave. The validity and the limitations of this approximation were discussed by Adams et al. (1998) and Tegze & Faigel (2001), and in particular by Bai (2003). Within the plane wave approximation, it is assumed that  $|\mathbf{u}| \ll |\mathbf{r}'_{\ell}|$ , where  $\mathbf{u} = \mathbf{r} - \mathbf{r}'_{\ell}$ , and the denominator in equation (1.8) is approximated with  $|\mathbf{R}_i - \mathbf{r}| \approx |\mathbf{R}_i - \mathbf{r}'_{\ell}|$ . In the exponent  $|\mathbf{R}_i - \mathbf{r}|$  is approximated with  $|\mathbf{R}_i - \mathbf{r}| \approx |\mathbf{v}| - \hat{\mathbf{v}} \cdot \mathbf{u}$ , where  $\mathbf{v} = \mathbf{R}_i - \mathbf{r}'_{\ell}$  and  $\hat{\mathbf{v}} = \mathbf{v}/|\mathbf{v}|$  [see also figure 1.2(b)]. Equation (1.8) can be rewritten as

$$\chi(\mathbf{k}) = -2r_{\rm e} \operatorname{Re}\left[\sum_{\ell} \frac{f_{\ell}(\mathbf{k}, \mathbf{k}_{\ell})}{|\mathbf{R}_i - \mathbf{r}'_{\ell}|} \mathrm{e}^{\mathrm{i}[k|\mathbf{R}_i - \mathbf{r}'_{\ell}| + \mathbf{k} \cdot (\mathbf{R}_i - \mathbf{r}'_{\ell})]}\right],\tag{1.10}$$

where  $f_{\ell}(\mathbf{k}, \mathbf{k}_{\ell}) = \int \rho_{\ell}(\mathbf{u}) e^{-i(\mathbf{k}+\mathbf{k}_{\ell})\cdot\mathbf{u}} d\mathbf{u}$  is the standard atomic form factor,<sup>1</sup>  $\mathbf{k}_{\ell} = k\hat{\mathbf{v}}$  and we have once again neglected the polarization term. Equation (1.10) is the simplest, yet accurate expression which can be obtained for an x-ray fluorescence hologram. We will be using (1.10) in the rest of the text to calculate monochromatic holograms for different types of atomic structures.

In the derivation of equations (1.8) and (1.10) we have neglected, without lose of generality, terms proportional to  $\sim 1/(kr)$  and  $\sim 1/(kr)^2$ . These terms have been actually dropped in equation (1.3) which gives the dipole radiation of an electron interacting with a electromagnetic field. They are responsible for so called near-field effects in XFH (Bai 2003).

As an example we have calculated numerically two holograms which are presented in figures 1.2(c) and 1.2(d). The hologram in figure 1.2(c) was simulated for a detector atom - point scatterer system with equation (1.9). The hologram in figure 1.2(d) was calculated with equation (1.10) for a detector atom - gallium scattering atom. In both cases the detector atom was located at the origin  $\mathbf{R}_i = (0, 0, 0)$  and the scattering objects were located at (0, 0, 3.19 Å). The beam energy was set to E = 16.0 keV ( $k = 8.12 \text{ Å}^{-1}$ ). In both holograms we can clearly see interference fringes which extend to the whole sphere. All the rings are centered along the straight line determined by the  $\mathbf{r}'$  (or  $\mathbf{r}'_{\ell}$ ) vector and they lay in planes that are parallel to this line. For the gallium scatterer note the fading of the hologram along the meridians which is due to the Ga form factor. The amplitudes of the holograms are very small. For the electron scatterer  $\chi \sim 2r_e/r' \sim 10^{-5}$ . For the gallium atom the amplitude is larger by a factor of Z = 31, i.e., the atomic number of Ga and  $\chi \sim 2r_eZ/r' \sim 10^{-4}$ .

<sup>&</sup>lt;sup>1</sup>Throughout this text, in all numerical calculations, the atomic from factor is approximated by a sum of five Gaussian functions and a constant term (Waasmaier & Kirfel 1995).

As another example, we have calculated a hologram for GaAs and chosen the gallium atom as the detector atom. It is presented in figure 1.2(e) and differs significantly from the holograms for simple atom - one scatterer systems. While the holograms for the simple systems are composed from clearly visible interference fringes, the GaAs hologram is composed from a number of dark/bright spots and sharp lines. The lines are known in literature as Kossel (normal mode of XFH) or x-ray standing wave lines (inverse mode of XFH) and we will discuss them in a while. The reader might be bewildered by the appearance of such a rich structure in the GaAs hologram. It can be, however, simply exampled by means of the Fourier series were one adds smooth sine and cosine functions to obtain in the end a complicated shape. Equation (1.10) does just that. It adds cosine functions on a sphere with different frequencies and amplitudes.

In GaAs, there is only one crystallographically nonequivalent site of gallium. It suffices to point  $\mathbf{R}_i$  to the position of one of the gallium atoms and one obtains a hologram of the GaAs structure as seen from the position of the gallium atoms. In many cases, however, atoms of the same element may occupy a fixed number of  $n_d$  crystallographically nonequivalent sites. These sites can be described by a set S of  $\mathbf{R}_i$  vectors, namely  $S \in {\mathbf{R}_i^1, \mathbf{R}_i^2, ..., \mathbf{R}_i^{n_d}}$ . To calculate a hologram in such a case one simply generates  $n_d$  holograms, one for each  $\mathbf{R}_i$  vector from S, and then averages them.

# HOLOGRAMS IN RECIPROCAL SPACE

Expression (1.10) for the hologram involves a sum over atoms which make up the considered atomic system. The summation is performed in real space, i.e., one needs the exact positions of the scatterers with respect to the detector atom to evaluate the sum in (1.10). For systems with long range order (crystals) it is also possible to give an expression for  $\chi_i$  in reciprocal space (Adams et al. 1998, Marchesini et al. 2002). To do so one needs to express the electron density as a Fourier series

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{H}} F_{\mathbf{H}} \mathrm{e}^{\mathrm{i}\mathbf{H}\cdot\mathbf{r}},\tag{1.11}$$

where **H** is the reciprocal lattice vector,  $F_{\mathbf{H}}$  are the Fourier coefficients (structure factors) and V is the unit cell volume. The next step is to substitute equation (1.11) into equation (1.8) and perform the integration over d**r**. Once again polarization is neglected. The result is

$$\chi_{i}(\mathbf{k}) = -\frac{2r_{e}}{V} \sum_{\mathbf{H}} F_{\mathbf{H}} \operatorname{Re} \left[ \int e^{i\mathbf{H}\cdot\mathbf{r}} \frac{e^{ik|\mathbf{R}_{i}-\mathbf{r}|}}{|\mathbf{R}_{i}-\mathbf{r}|} e^{i\mathbf{k}\cdot(\mathbf{R}_{i}-\mathbf{r})} d\mathbf{r} \right]$$
$$= -\frac{8\pi r_{e}}{V} \sum_{\mathbf{H}} F_{\mathbf{H}} e^{i\mathbf{H}\cdot\mathbf{R}_{i}} \frac{1}{|\mathbf{k}-\mathbf{H}|^{2}-k^{2}}$$
(1.12)

and it is actually divergent at the Bragg condition. This divergence appears since extinction, mosaicity and the finite crystal size are neglected. These can be approximated by writing k as a complex number, i.e.,  $k \mapsto k + i\Gamma$  (Marchesini et al. 2002). Equation (1.12) then yields (Adams et al. 1998, Marchesini et al. 2002)

$$\chi_i(\mathbf{k}) = -\frac{8\pi r_{\rm e}}{V} \operatorname{Re} \sum_{\mathbf{H}} F_{i\mathbf{H}} \left[ \chi_{\mathbf{H}}^R(\mathbf{k}) + \mathrm{i}\chi_{\mathbf{H}}^I(\mathbf{k}) \right], \qquad (1.13)$$

where

$$\chi_{\mathbf{H}}^{R}(\mathbf{k}) = \frac{|\mathbf{H}|^{2} + 2\mathbf{H} \cdot \mathbf{k}}{(|\mathbf{H}|^{2} + 2\mathbf{H} \cdot \mathbf{k})^{2} + (2k\Gamma)^{2}} \quad \text{and} \quad \chi_{\mathbf{H}}^{I}(\mathbf{k}) = \frac{2k\Gamma}{(|\mathbf{H}|^{2} + 2\mathbf{H} \cdot \mathbf{k})^{2} + (2k\Gamma)^{2}}.$$
 (1.14)

In equation (1.13) the structure factors were redefined to  $F_{i\mathbf{H}} = F_{\mathbf{H}} e^{i\mathbf{H}\cdot\mathbf{R}_i}$ . If atoms of a certain element occupy  $n_d$  crystallographically nonequivalent sites in the unit cell then each such position s in the unit cell is given by a  $\mathbf{R}_i^s$  vector. To calculate a hologram from a certain element i one has to calculate  $\chi_i$  for each of these sites and average the resulting holograms. This is equivalent to redefining the structure factors as

$$F_{i\mathbf{H}} = \frac{1}{n_d} F_{\mathbf{H}} \sum_{s} e^{i\mathbf{H} \cdot \mathbf{R}_i^s}, \qquad (1.15)$$

where the s sum runs over the crystallographically nonequivalent sites in the unit cell occupied by element i.

Equation (1.13) gives an expression for  $\chi_i$  in reciprocal space. Using Friedel's law  $(F_{\mathbf{H}} = F_{-\mathbf{H}}^*)$  it can be written as

$$\chi_i(\mathbf{k}) = -\frac{4\pi r_{\rm e}}{V} \sum_{\mathbf{H}} \left[ \operatorname{Re}(F_{i\mathbf{H}}) \chi_{\mathbf{H}}^+(\mathbf{k}) - \operatorname{Im}(F_{i\mathbf{H}}) \chi_{\mathbf{H}}^-(\mathbf{k}) \right], \qquad (1.16)$$

where

$$\chi_{\mathbf{H}}^{+}(\mathbf{k}) = \chi_{\mathbf{H}}^{R}(\mathbf{k}) + \chi_{-\mathbf{H}}^{R}(\mathbf{k}) \quad \text{and} \quad \chi_{\mathbf{H}}^{-}(\mathbf{k}) = \chi_{\mathbf{H}}^{I}(\mathbf{k}) + \chi_{-\mathbf{H}}^{I}(\mathbf{k}).$$
(1.17)

While equation (1.10) sums contributions from single atoms, equation (1.16) sums contributions from **H** vectors. It can be thought of as a sum of contributions from lattice planes.

The  $\chi_{\mathbf{H}}^{+}(\mathbf{k})$  function is plotted in figure 1.3(a) for **H** that corresponds to the  $(\bar{1}\bar{1}1)$  plane while  $\chi_{\mathbf{H}}^{-}(\mathbf{k})$  is plotted in figure 1.3(b) for **H** that corresponds to the  $(1\bar{1}1)$  plane. In both figures the intersection of the sphere with the plane that corresponds to **H** is marked with the solid white great circle. The  $\chi_{\mathbf{H}}^{+}(\mathbf{k})$  and  $\chi_{\mathbf{H}}^{-}(\mathbf{k})$  functions form bands that are centered at the mentioned great circles. The bands are composed out of two lines. These are the Kossel/x-ray standing wave lines that we have stumbled upon in figure 1.2(e). Equation (1.17) describes the shape of these lines in terms of the kinematical diffraction theory (Adams et al. 1998, Tolkiehn et al. 2005). The profiles of these lines along the dashed great circles in figures 1.3(a) and 1.3(b) are shown in figures 1.3(c) and 1.3(d). The distance along the dashed great circles is measured with the  $\Delta \alpha$  variable. The



Figure 1.3: (a) Plot of the  $\chi_{\mathbf{H}}^+(\mathbf{k})$  function for a cubic system and the  $(\bar{1}\bar{1}1)$  plane. The lattice constant was set to a = 3.75 Å and k = 8.8 Å<sup>-1</sup>. (b) Same as (a) but for  $\chi_{\mathbf{H}}^-(\mathbf{k})$  and the  $(1\bar{1}1)$  plane. (c) and (d) Profiles of  $\chi_{\mathbf{H}}^+(\mathbf{k})$  and  $\chi_{\mathbf{H}}^-(\mathbf{k})$  along the dashed great circles in (a) and (b), respectively. The Bragg angle is marked with  $\alpha_{\mathbf{B}}$ . (e) Detailed profiles of  $\chi_{\mathbf{H}}^+(\Delta\alpha)$  and  $\chi_{\mathbf{H}}^-(\Delta\alpha)$  in the vicinity of  $\Delta\alpha = 0$ . (f) Cones determined by the Bragg condition.

shape of the lines in the vicinity of  $\Delta \alpha = 0$  is plotted in figure 1.3(e). The lines either change sign  $[\chi_{\mathbf{H}}^+(\Delta \alpha)]$  or have an maximum/minimum  $[\chi_{\mathbf{H}}^-(\Delta \alpha)]$  at the Bragg condition which is given by the angle  $\alpha_{\mathrm{B}} = \arcsin[|\mathbf{H}|/(2k)]$ . The Bragg condition defines a cone whose opening angle is equal to  $\pi - 2\alpha_{\mathrm{B}}$ , see figure 1.3(f). The lines are centered at the edge of the base of the cone.

The appearance of the lines at and close to the Bragg conditions can be understood intuitively. At the Bragg condition the incident x-ray waves and the scattered waves add up constructively and form a spatially modulated standing x-ray wave field. In principle, the detector atom can be placed anywhere in this field and experiences either a stronger or weaker x-ray intensity. The detector atom either detects greater or lesser amount of photons depending on its position relative to the crystal lattice.

# 1.2 A DIFFERENT POINT OF VIEW - XFH AS AN ABSORPTION TECHNIQUE

X-ray fluorescence holography in the inverse mode is based on the internal detector concept. In the previous section we have calculated the wave field intensity at the position of the detector atom and we have shown that it contains a holographic term. There is, however, a different, yet complementary point of view which treats XFH as an absorption technique (Miller & Sorensen 1997, Nishino & Materlik 1999). This concept can be linked to the anomalous absorption effect first observed by Borrmann (1950). In his work he observed as sharp decrease in the absorption of x-rays when the Bragg condition was fulfilled. Other dramatic changes in the absorption of x-rays can be observed during the formation of x-ray standing waves (Batterman & Cole 1964). The possibility of deriving atomic structure information from absorption effects was already suggested by Cowley (1964).

From the point of view of absorption, the hologram is regarded as a direction and energy dependent part of the photoionisation cross section  $\sigma_i$  of an absorbing atom, namely (Nishino & Materlik 1999)

$$\sigma_i(\mathbf{k}) = \sigma_i^0(k) \left[ 1 + \chi_i(\mathbf{k}) \right], \tag{1.18}$$

where  $\sigma_i^0(E)$  is the photoionisation cross section of an isolated atom of kind *i*. Consider once again figure 1.2(a). The holographic term arises due to photon interference between the incident x-ray wave and waves scattered from neighbors of the absorbing (detector) atom. These waves can add up either constructively or destructively and influence the matrix elements which are responsible for absorption. According to the Fermi's golden rule the photoionisation cross section  $\sigma_i$  is proportional to the square of the matrix element  $\langle f | \mathcal{H}_I | h \rangle$  which describes the transition rate between the initial state  $|h\rangle$  and the final state  $|f\rangle$  (Sakurai 1994, Als-Nielsen & McMorrow 2011). The interaction Hamiltonian  $\mathcal{H}_I = \mathbf{p} \cdot \mathbf{A}$  describes the interaction between the atom and the electromagnetic wave field which is represented by the vector potential  $\mathbf{A}$ . Effectively, there are two waves and  $\mathbf{A}$  can be

written as  $\mathbf{A} = \mathbf{A}_p + \mathbf{A}_s$ , where  $\mathbf{A}_p$  represents the vector potential of a plane wave and  $\mathbf{A}_s$  of the scattered wave. The square of the matrix element can be written as

$$\sigma_{i} \propto |\langle f|\mathcal{H}_{I}|h\rangle|^{2} = [\langle f|\mathbf{p}\cdot\mathbf{A}_{p}|h\rangle + \langle f|\mathbf{p}\cdot\mathbf{A}_{s}|h\rangle] [\langle f|\mathbf{p}\cdot\mathbf{A}_{p}|h\rangle + \langle f|\mathbf{p}\cdot\mathbf{A}_{s}|h\rangle]^{*}$$
$$= |\langle f|\mathbf{p}\cdot\mathbf{A}_{p}|h\rangle|^{2} \left[1 + \left\{\frac{\langle f|\mathbf{p}\cdot\mathbf{A}_{p}|h\rangle\langle f|\mathbf{p}\cdot\mathbf{A}_{s}|h\rangle^{*}}{|\langle f|\mathbf{p}\cdot\mathbf{A}_{p}|h\rangle|^{2}} + \text{c.c.}\right\}\right], \qquad (1.19)$$

where in the second line we have neglected  $|\langle f | \mathbf{p} \cdot \mathbf{A}_s | h \rangle|^2$  and c.c. stand for *complex conjugate*. The first term  $|\langle f | \mathbf{p} \cdot \mathbf{A}_p | h \rangle|^2$  can be identified as  $\sigma_i^0$  while the second term is proportional to  $\chi_i$ , i.e.,

$$\chi_i \propto \langle f | \mathbf{p} \cdot \mathbf{A}_s | h \rangle^*. \tag{1.20}$$

Just to put XFH into perspective among other absorption methods that can be used for atomic structure determination we mention that XFH is in a way similar to x-ray absorption fine structure (XAFS) [Bunker (2010)]. In XAFS the atom absorbs a photon from the incoming x-ray wave and emits a photoelectron. As the photoelectron wave function propagates it is back scattered from neighboring atoms and returns to the atom from which it was emitted. The interference of the outgoing and returning photoelectron waves can be constructive or destructive as in the case of photons and also modifies the matrix element. To take XAFS and XFH into account at the same time one can write  $\langle f + \Delta f | \mathbf{p} \cdot (\mathbf{A}_p + \mathbf{A}_s) | h \rangle$ , where  $|\Delta f \rangle$  is the modification of the final state due to the back scattered photoelectron. Together with the XAFS oscillation the photoionisation cross section can be written as (Nishino & Materlik 1999)

$$\sigma_i(\mathbf{k}) = \sigma_i^0(k) \left[ 1 + \chi_i^e(k) + \chi_i(\mathbf{k}) \right], \qquad (1.21)$$

where  $\chi_i^e$  is the XAFS oscillation. The two oscillations in (1.21) are present simultaneously in XAFS spectra and the holographic part is in this case referred to as the *photon interference x-ray absorption* fine structure ( $\pi$ XAFS) [Tröger et al. (2001), Nishino et al. (2001)].

# 1.3 Measuring an X-ray fluorescence hologram in practice

The hologram is a fractional change of the photoionisation cross section  $\sigma_i$ . In order to measure  $\chi_i$  one has to measure a quantity that is somehow related to  $\sigma_i$ . In other words one has to measure a quantity that is related to absorption. The measurements have to be performed as a function of **k**. One can chose and measure, e.g., photoelectrons or Auger electrons. In XFH, as the name suggests, one measures x-ray fluorescence.

A typical XFH experimental setup is presented in figure 1.4. An x-ray beam illuminates a flat sample. The propagation direction of the beam is fixed. The sample-detector assembly is rotated around the  $\mathcal{R}$  axis so that the  $\theta$  angle changes. The sample is rotated around its surface normal and this rotation is given by the  $\phi$  angle. The angular position of the detector is given by  $\theta_0$  and is fixed throughout the measurement. In the process of rotation the detector measures x-ray fluorescence as a function of  $\theta$  and  $\phi$ .

Lets assume that one is interested in the atomic structure around a specific element i in the sample. Then one sets the energy of the incident x-ray beam above a given absorption edge, e.g., the K edge (for heavier elements the L edges can be used) and measures fluorescence through a chosen emission line  $\lambda$ , e.g., K $\alpha$ . Let us further assume that the sample can be treated as thin. In this case the number of fluorescence photons  $Y_{i,\lambda}$  emitted by element i through the  $\lambda$  emission line will be proportional to the number of photons per second  $I_0(E)$  hitting the sample, the photoionisation cross section  $\sigma_i$  and the path  $T/\cos\theta$  that the beam travels inside the sample (T is the sample's thickness).  $Y_{i,\lambda}$  can be written as (Beckhoff et al. 2006)

$$Y_{i,\lambda}(E,\theta,\phi) = g_{i,\lambda} \frac{T}{\cos\theta} I_0(E) \omega_{iS} F_{i\lambda} \sigma_i^0(E) [1 + \chi_i(E,\theta,\phi)], \qquad (1.22)$$

where  $g_{i,\lambda}$  is a detector dependent constant,  $\omega_{iS}$  is the fluorescence yield of shell S,  $F_{i\lambda}$  is the fractional radiative rate of the  $\lambda$  emission line and E is the incident beam energy. Equation (1.22) can be rewritten as

$$Y_{i,\lambda}(E,\theta,\phi) = Y_{i,\lambda}^0(E,\theta)[1+\chi_i(E,\theta,\phi)], \qquad (1.23)$$

where

$$Y_{i,\lambda}^{0}(E,\theta) = g_{i,\lambda}TI_{0}(E)\omega_{iS}F_{i,\lambda}\sigma_{i}^{0}(E)/\cos\theta.$$
(1.24)

From the experimental point of view, equation (1.23) is one of the basic equations of XFH. It is used in experiments to extract the holographic signal from the measured number of fluorescence photons (Hayashi et al. 2012). It consists of two term: a slowly varying term  $Y_{i,\lambda}^0$  and a very small rapidly oscillating term  $Y_{i,\lambda}^0 \chi_i$ . If the slowly varying term can be somehow estimated, e.g., by appropriate fitting procedures, then  $\chi_i$  can be calculated as

$$\chi_i(E,\theta,\phi) = \frac{Y_{i,\lambda}(E,\theta,\phi) - Y_{i,\lambda}^0(E,\theta)}{Y_{i,\lambda}^0(E,\theta)}.$$
(1.25)

The procedure of background fitting and the retrieval of  $\chi_i$  from  $Y_{i,\lambda}$  by means of equation (1.25) is closely related to data reduction procedures in XAFS (Bunker 2010).

The holographic signal is very small  $(\chi \sim 10^{-4})$  (see Sec. 1.1) and this introduces some difficulties in practical measurements. Hence, to retrieve the hologram from  $Y_{i,\lambda}(\theta, \phi)$  at least a few times  $10^6$  photons need to be measured per one  $(\theta, \phi)$  pixel. This makes the measuring times long even with intense x-ray sources and high count rate detectors. In the pioneering experiments the measurement time for a single hologram was 150 hours Gog et al. (1996). In a recent experiment, at the BL22XU beamline at SPring-8, the measurement time for a single hologram was cut down to

just 3 hours (Hu et al. (2014) - supplementary material). To measure x-ray fluorescence the authors have used an avalanche photodiode, a fast detector with a maximum count rate of  $10^8$  counts per second. In laboratory conditions the measurement times for a single hologram are a matter of days (Takahashi et al. 2004, Dabrowski & Korecki 2012).



Figure 1.4: A typical experimental setup for XFH measurements. An x-ray beam illuminates a flat sample. The whole sample-detector assembly is rotated with respect to the incoming beam around the  $\mathcal{R}$  axis. The sample is additionally rotated around its normal. The relative position of the sample with respect to the beam is given by a pair of angles, namely  $(\theta, \phi)$ . The  $\theta_0$  angle gives the angular position of the detector and is fixed throughout the measurement. The detector measures x-ray fluorescence emitted form the sample.

### 1.4 DATA PRESENTATION

The holographic signal  $\chi_i$  is a function of the vector  $\mathbf{k} = (k_x, k_y, k_z)$ , or equivalently, of the  $\theta$ and  $\phi$  angles and the beam energy E. The connection between these reads  $k_x = k \sin \theta \cos \phi$ ,  $k_y = k \sin \theta \sin \phi$ ,  $k_z = k \cos \theta$  and  $k [\text{Å}^{-1}] = 0.5068 E[\text{keV}]$  is the standard wave number energy conversion. On the one hand, it is most convenient to represent  $\chi_i$  on the surface of a sphere. On the other hand, presenting a full sphere on a flat sheet of paper or computer screen is highly inconvenient. A much better way is to map the surface of a sphere onto the flat surface of a sheet of paper or screen by using one of the many cartographic projections. In this work we will present holographic data in the Lambert azimuthal equal-area projection (Borradaile 2010).

#### 1. X-RAY FLUORESCENCE HOLOGRAPHY (XFH)

Each point on a sphere can be represented by a unit vector  $\hat{\mathbf{k}} = \mathbf{k}/|\mathbf{k}| = (\hat{k}_x, \hat{k}_y, \hat{k}_z)$ . In the Lambert azimuthal equal-area projection each point on the sphere is mapped to a corresponding point on a plane which is given by  $\mathbf{v} = (v_x, v_y)$ . The mapping is defined as

$$v_x = \hat{k}_x \sqrt{\frac{2}{1+\hat{k}_z}}$$
 and  $v_y = \hat{k}_y \sqrt{\frac{2}{1+\hat{k}_z}}$ . (1.26)

To give the reader a sens of how the holograms will be represented from now on an example mapping of this type is show in figure 1.5.



Figure 1.5: (a) A schematic explanation of the *Lambert azimuthal equal-area projection* used in this work for data presentation. Each point of the sphere is projected onto a plane along an arc whose center is at S. (b) Two examples of the projection for earth (top) and a hologram (bottom) from figure 1.2(b). In both cases only the northern hemisphere is projected.

### 1.5 Atomic structure reconstruction

# HOLOGRAPHIC RECONSTRUCTION

The main feature of holography, that makes it so appealing, is its sensitivity to the phase of the scattered radiation. This allows the reconstruction of the imaged object in three dimensions. In optical holography this is achieved by illuminating the hologram with the reference wave R that was used to record it (see figure 1.6). The hologram can be characterized by a transmittance  $\mathcal{T}$  which is proportional to I. The wave transmitted through the hologram will be proportional to (Gabor 1949)

$$R\mathcal{T} \propto R|R+O|^2 = |R_0|^2 \left[ R_0 + O_0 \mathrm{e}^{\mathrm{i}(\phi_R - \phi_O)} + O_0 \mathrm{e}^{-\mathrm{i}(\phi_R - \phi_O)} + |O_0|^2 / R_0 \right].$$
(1.27)

The first term represents the directly transmitted illuminating reference wave. The last term is negligible since the object wave is assumed to be much weaker then the reference wave. What is important are the second and third terms. The second term is the reconstruction of the original object. The third term, which is a complex conjugate of the second term, is the virtual (twin) image of the original object.



Figure 1.6: Reconstruction of an inline hologram.

In XFH the process of reconstruction boils down to printing the hologram on a sphere and illuminating it with a converging spherical wave. In practice this can only be achieved on a computer through a numerical calculation. The reconstruction yields a three dimensional image of the atomic structure around the absorbing atom. The most basic holographic reconstruction scheme was proposed by Barton (1988, 1991). This approach is based on the Helmholtz-Kirchhoff integral theorem which states that the wave field amplitude inside a closed surface S can be calculated, provided that the value of the wave field at the enclosing surface is known. In XFH the enclosing surface is simply the hologram and the wave field U at position  $\mathbf{r}$  is given by (Barton 1988)

$$U_i(\mathbf{r}) = \int_S \chi_i(\mathbf{k}) \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \mathrm{d}\Omega, \qquad (1.28)$$

where the integration is over the whole sphere. An example reconstruction obtained with equation (1.28) is shown in figure 1.7(a). The reconstruction was performed in the xz plane for the hologram from figure 1.2(d). Two distinct maxima can be see in the reconstruction image. The top one corresponds to the actual position (true image) of the scattering atom. The bottom one is a twin (virtual) image which is analogous to the twin images in optical holography. Twin images pose a serious problem in XFH. They make the interpretation of results ambiguous. Most importantly, if a virtual image will appear at the position of a true image the two can cancel themselves out for certain beam energies (Len et al. 1994).

The twin image problem can be solved by multiple energy XFH (Gog et al. 1996). In this case the reconstruction is performed from a set of holograms, each measured for a different beam energy,



Figure 1.7: Holographic reconstruction in the xz plane of the system of atoms in figure 1.2(d). (a) Reconstruction from a single hologram at E = 16.0 keV. (b) Reconstruction from a set of 7 holograms. The holograms were generated for energies from 14.5 keV to 17.5 keV with a step of 0.5 keV. In both images  $|U(\mathbf{r})|$  is shown and the position of the absorbing atom is marked with a cross.

and equation (1.28) is extended to the third dimension, namely (Barton 1991)

$$U_i(\mathbf{r}) = \int \chi_i(\mathbf{k}) \mathrm{e}^{-\mathrm{i}(kr + \mathbf{k} \cdot \mathbf{r})} \mathrm{d}^3 \mathbf{k}.$$
 (1.29)

Now, the integration is over the whole volume of **k** space. The additional term  $e^{-ikr}$  shifts the phase of the twin image while keeping the phase of the true image constant. As a result of integration over dk the true image is strengthened whereas the twin image is suppressed. An example reconstruction by means of equation (1.29) is presented in figure 1.7(b) again for the system of atoms from figure 1.2(d). We see that the twin image is strongly suppressed. The integral over dk was approximated by a sum over 7 values of the beam energy from 14.5 keV to 17.5 keV with a step of 0.5 keV. For each of these values separate holograms were generated. Had we taken more holograms in the approximation of the dk integral, the twin image would be completely absent. A comparison of reconstructions from single energy holograms and from multiple energy hologram sets can be found in (Len, Gog, Fadley & Materlik 1997).

Seemingly taking more holograms is not a problem. In practice, however, the integral over dk is approximated by a rather small sum of holograms due to the long measurement times of holograms. An interesting possibility of twin image removal was proposed by Nishino et al. (2002), where by an appropriate choice of wave vectors in the sum over dk the twin images were significantly suppressed with just two holograms. The suppression was at least 40%. In general, however, more than two holograms are required for twin image removal.

# A LINEAR REGRESSION APPROACH

Apart from the holographic reconstruction it is also possible to use a linear regression algorithm to solve crystal structures with XFH. This approach was proposed by Chukhovskii & Poliakov (2003) and is based on equation (1.16). It uses Kossel lines to determine both the amplitude and phase of the structure factors. Actually, the possibility that Kossel lines may be used to obtain phase information was already mentioned nearly 40 years ago by Hannon et al. (1974) in a paper that dealt with Mössbauer diffraction.

Equation (1.16) is a linear combination of the  $\chi_{\mathbf{H}}^+$  and  $\chi_{\mathbf{H}}^-$  functions and a generalized linear least squares approach (Press et al. 2002) can be used to fit the real and imaginary parts of  $F_{i\mathbf{H}}$ . For this we represent the hologram as a  $N \times M$  matrix whose elements are  $(\chi_i)_{nm}$ , where  $n \in \{1, 2, 3, ..., N\}$ and  $m \in \{1, 2, 3, ..., M\}$ . We rewrite equation (1.16) as

$$(\chi_i)_{nm} = -\frac{4\pi r_{\mathbf{e}}}{V} \sum_{\mathbf{H}} [\operatorname{Re}(F_{i\mathbf{H}})(\chi_{\mathbf{H}}^+)_{nm} - \operatorname{Im}(F_{i\mathbf{H}})(\chi_{\mathbf{H}}^-)_{nm}]$$
(1.30)

and define the following system of equations

$$(\mathbf{W}^{\mathrm{T}}\mathbf{W})\mathbf{F} = \mathbf{W}^{\mathrm{T}}\mathbf{b},\tag{1.31}$$

where T denotes the transpose of a matrix. The **b** vector is filed with the values of  $(\chi_i)_{nm}$ , i.e.,  $\mathbf{b}^{\mathrm{T}} = [(\chi_i)_{11}, (\chi_i)_{12}, (\chi_i)_{13}, ..., (\chi_i)_{N(M-1)}, (\chi_i)_{NM}]$ . The columns of the **W** matrix are filed with values of the  $(\chi_{\mathbf{H}}^+)_{nm}$  and  $(\chi_{\mathbf{H}}^-)_{nm}$  functions in the following way

$$\mathbf{W}^{\mathrm{T}} = \begin{pmatrix} (\chi_{\mathbf{H}_{1}}^{+})_{11} & (\chi_{\mathbf{H}_{1}}^{+})_{12} & (\chi_{\mathbf{H}_{1}}^{+})_{13} & \cdots & (\chi_{\mathbf{H}_{1}}^{+})_{N(M-1)} & (\chi_{\mathbf{H}_{1}}^{+})_{NM} \\ (\chi_{\mathbf{H}_{2}}^{+})_{11} & (\chi_{\mathbf{H}_{2}}^{+})_{12} & (\chi_{\mathbf{H}_{2}}^{+})_{13} & \cdots & (\chi_{\mathbf{H}_{2}}^{+})_{N(M-1)} & (\chi_{\mathbf{H}_{2}}^{+})_{NM} \\ \vdots & & \ddots & & \vdots \\ (\chi_{\mathbf{H}_{L}}^{+})_{11} & (\chi_{\mathbf{H}_{L}}^{+})_{12} & (\chi_{\mathbf{H}_{L}}^{+})_{13} & \cdots & (\chi_{\mathbf{H}_{L}}^{+})_{N(M-1)} & (\chi_{\mathbf{H}_{L}}^{+})_{NM} \\ (\chi_{\mathbf{H}_{1}}^{-})_{11} & (\chi_{\mathbf{H}_{1}}^{-})_{12} & (\chi_{\mathbf{H}_{1}}^{-})_{13} & \cdots & (\chi_{\mathbf{H}_{1}}^{-})_{N(M-1)} & (\chi_{\mathbf{H}_{1}}^{-})_{NM} \\ \vdots & & \ddots & & \vdots \\ (\chi_{\mathbf{H}_{L}}^{-})_{11} & (\chi_{\mathbf{H}_{2}}^{-})_{12} & (\chi_{\mathbf{H}_{2}}^{-})_{13} & \cdots & (\chi_{\mathbf{H}_{2}}^{-})_{N(M-1)} & (\chi_{\mathbf{H}_{2}}^{-})_{NM} \end{pmatrix}.$$
(1.32)

The sum in equation (1.30) runs over infinitely many **H** vectors. This implies, that in principle, the **W** matrix should have infinitely many rows. This is impractical and in real applications the amount of **H** vectors is reduced to a finite number. In equation (1.32) it is assumed that one takes L vectors when performing the sum in equation (1.30). The **F** vector contains the real and imaginary parts of the structure factors

$$\mathbf{F}^{\mathrm{T}} = -\frac{4\pi r_{\mathrm{e}}}{V} [\operatorname{Re}(F_{i\mathbf{H}_{1}}), \operatorname{Re}(F_{i\mathbf{H}_{2}}), ..., \operatorname{Re}(F_{i\mathbf{H}_{L}}), \operatorname{Im}(F_{i\mathbf{H}_{1}}), \operatorname{Im}(F_{i\mathbf{H}_{2}}), ..., \operatorname{Im}(F_{i\mathbf{H}_{L}})].$$

Equation (1.31) is a standard least-squares estimate for the unknown parameters  $\operatorname{Re}(F_{i\mathbf{H}})$  and  $\operatorname{Im}(F_{i\mathbf{H}})$  in equation (1.30). The real and imaginary parts of  $F_{i\mathbf{H}}$  can be obtained by solving equation (1.31). Once the structure factors are determined the electron density can be calculated with equation (1.11).

Please note that the reconstruction by means of equation (1.16) is qualitatively different from the holographic reconstruction [equations (1.28) or (1.29)]. Only the long range order component of the electron density can be obtained with (1.16) whereas the holographic reconstruction focuses on atomic arrangements around the absorbing atom, i.e., on local atomic structure. Moreover, the holographic reconstruction is a model free approach, i.e., it does not require any *a priori* knowledge about the structure. When using equation (1.16) one must have access to the shape of the unit cell. This information has to be obtained by other means or it has to be determined from the hologram before the fitting procedure. Despite these drawbacks the reconstruction based on (1.16) is a useful tool if only one hologram is available which is typical for laboratory experiments.

#### OTHER RECONSTRUCTION APPROACHES

Apart from the holographic reconstruction and the linear regression approach a few other reconstruction methods have been proposed. Worth mentioning is the work of Marchesini & Fadley (2003) where the hologram reconstruction is treated as a deconvolution problem. The authors apply a few iterative deconvolution methods and attempt to retrieve the electron density from the x-ray fluorescence hologram. Another approach which was developed for electron holography and can be applied to XFH is the maximum entropy reconstruction scheme (Matsushita et al. 2005, 2007). The most recent development by Wang et al. (2012) is based one the decomposition of holograms into spherical harmonics to extract the structure factors.

### Chapter 2

# WHITE BEAM XFH AND WAVELETS

So far, we have assumed that a monochromatic x-ray beam is used in XFH experiments. Such experiments can be also performed with polychromatic radiation. The first holographic experiment, in the inverse mode, in which a polychromatic x-ray beam was used was performed by Korecki & Materlik (2001). The holographic pattern was measured for a Si photodiode which served simultaneously as a sample and detector. The incident white beam was generated by a bending magnet and the absorption of the diode was monitored by measuring its photocurrent. Apart from a proof of principle demonstration that a white x-ray beam can be successfully used to record atomic resolution holograms, it was shown that white beam holograms can be regarded as quasi real space projections of the crystal structure around absorbing atoms. This was a unique result since diffractive methods probe the reciprocal space.

Subsequent work in the area of white beam holography focused on structure retrieval procedures. The tomographic algorithm was proposed and validated on data measured for the GaP crystal (Korecki et al. 2006*b*,*a*) whereas the wavelet approach was tested on data measured for InAs (Korecki, Novikov & Tolkiehn 2009). In both of these experiments the holograms were measured with the total electron yield and did not provide element sensitive information. The first experiment in which a polychromatic x-ray beam together with x-ray fluorescence was used was preformed for Nb atoms in LiNbO<sub>3</sub> (Korecki et al. 2011). It marked the beginning of white beam XFH. These three experiments also utilized hard x-ray radiation and were conducted on synchrotron sources. A laboratory white beam XFH experiment was reported only recently by Dabrowski et al. (2013). A recent review of atomic resolution holography with white x-rays can be found in (Korecki, Tolkiehn & Novikov 2009).

All the mentioned experiments were feasibility studies. They provided the basic theoretical framework for the description of experiments and the first structure retrieval procedures. Here we extend some of the mentioned results, in particular the wavelet approach. This chapter is based on the work of Dul & Korecki (2012).

# 2.1 WHITE HOLOGRAMS

Let us assume the same experimental setup as in Section 1.3 but instead of a monochromatic beam we will now be using a polychromatic one. The sample is assumed to be sufficiently thin so than equation (1.23) holds. When a polychromatic beam of x-rays is used in XFH experiments equation

(1.23) needs to be integrated over energy

$$\bar{Y}_{i,\lambda}(\theta,\phi) = \int_0^\infty Y_{i,\lambda}^0(E,\theta) \left[1 + \chi_i(E,\theta,\phi)\right] dE$$
$$= \bar{Y}_{i,\lambda}^0(\theta) \left[1 + \bar{\chi}_i(\theta,\phi)\right], \qquad (2.1)$$

where

$$\bar{Y}^{0}_{i,\lambda}(\theta) = \int_{0}^{\infty} Y^{0}_{i,\lambda}(E,\theta) \mathrm{d}E$$
(2.2)

and

$$\bar{\chi}_i(\theta,\phi) = \frac{1}{\int_0^\infty I_0(E)\sigma_i^0(E)\mathrm{d}E} \int_0^\infty I_0(E)\sigma_i^0(E)\chi_i(E,\theta,\phi)\mathrm{d}E.$$
(2.3)

 $I_0$  now describes the incident energy spectrum and is given in units of photons/s/keV. As for monochromatic x-rays, equation (2.1) is one of the basic equations of white beam XFH. It is used to retrieve white holograms  $\bar{\chi}_i$  from the measured fluorescence according to

$$\bar{\chi}_i(\theta,\phi) = \frac{\bar{Y}_{i,\lambda}(\theta,\phi) - \bar{Y}_{i,\lambda}^0(\theta)}{\bar{Y}_{i,\lambda}^0(\theta)}.$$
(2.4)

In the process of  $\bar{\chi}_i$  retrieval the slowly varying background  $\bar{Y}^0_{i,\lambda}$  needs to be estimated which is usually done by appropriate fitting procedures. At this point we define the effective spectrum  $N_i(E)$ as

$$N_i(E) = I_0(E)\sigma_i^0(E).$$
(2.5)

With this definition we can rewrite expression (2.3) for  $\bar{\chi}_i$  as

$$\bar{\chi}_i(\theta,\phi) = \int_0^\infty N_i(E)\chi_i(E,\theta,\phi)\mathrm{d}E.$$
(2.6)

In (2.6) we have assumed that N(E) is normalized<sup>1</sup> to unity i. e.  $\int_0^\infty N_i(E) dE = 1$ .

If we use equation (1.8) and substitute it into (2.6) together with equation (1.4) we can write

$$\bar{\chi}_{i}(\hat{\mathbf{k}}) = -2r_{e} \int_{0}^{\infty} N_{i}(k) \sum_{\ell} \operatorname{Re}\left[\int \rho(\mathbf{r} - \mathbf{r}_{\ell}') \frac{\mathrm{e}^{ik|\mathbf{R}_{i} - \mathbf{r}|}}{|\mathbf{R}_{i} - \mathbf{r}|} \mathrm{e}^{i\mathbf{k} \cdot (\mathbf{R}_{i} - \mathbf{r})} \mathrm{d}^{3}\mathbf{r}\right] \mathrm{d}k$$
(2.7)

or equivalently for a real valued electron density

$$\bar{\chi}_i(\hat{\mathbf{k}}) = -2r_{\rm e} \sum_{\ell} \int \frac{\rho(\mathbf{r} - \mathbf{r}_{\ell})}{|\mathbf{R}_i - \mathbf{r}|} h_i(\vartheta', |\mathbf{R}_i - \mathbf{r}|) \mathrm{d}\mathbf{r}, \qquad (2.8)$$

<sup>&</sup>lt;sup>1</sup>In fact even if N(E) is not normalized to unity equation (2.6) still holds. To show this we write  $N_i(E) = N_{i0}n_i(E)$ , where  $\int_0^\infty n_i(E)dE = 1$  and  $N_{i0}$  is the normalization constant. If we substitute this form of N(E) into  $\bar{\chi}_i$  in (2.3) we obtain equation (2.6) since  $N_{i0}$  cancels out.
where

$$h_i(\vartheta', |\mathbf{R}_i - \mathbf{r}|) = \operatorname{Re}\left[\int_{-\infty}^{\infty} N_i(k) \mathrm{e}^{\mathrm{i}k|\mathbf{R}_i - \mathbf{r}|(1 - \cos\vartheta')} \mathrm{d}k\right]$$
(2.9)

and  $\vartheta' = \arccos[-\hat{\mathbf{k}} \cdot (\mathbf{R}_i - \mathbf{r})/|\mathbf{R}_i - \mathbf{r}|]^2$  In equations (2.7) and (2.8) we have changed the integration from dE to dk and from  $(\theta, \phi)$  to  $\hat{\mathbf{k}}$ . In equation (2.9), we have also changed the lower limit of integration over dk from 0 to  $-\infty$ . This is possible because for realistic energy spectra  $N_i(k) = 0$ when  $k \leq 0$ . This change is dictated by convenience. In (2.7) we have also neglected the polarization factor P.

In principle, equation (2.7) could be used to conveniently calculate white beam holograms. However, its structure makes its application impractical. One needs to preform two integrals one over dr and a second one over dk. In most cases the integrals have to be evaluated numerically. For reasonable time frames these calculations are feasible only for systems which consist of a few atoms. For large system of atoms it is possible to use the plane wave approximation and simplify equation (2.7). If one makes the same assumptions as in the derivation of equation (1.10) one can write equation (2.7) as

$$\bar{\chi}_{i}(\hat{\mathbf{k}}) = -2r_{\mathrm{e}}\sum_{l} \frac{1}{|\mathbf{R}_{i} - \mathbf{r}_{\ell}'|} \operatorname{Re}\left[\int_{0}^{\infty} N_{i}(k) f_{l}(\mathbf{k}, \mathbf{k}_{\ell}) \mathrm{e}^{\mathrm{i}k|\mathbf{R}_{i} - \mathbf{r}_{\ell}'| + \mathrm{i}\mathbf{k} \cdot (\mathbf{R}_{i} - \mathbf{r}_{\ell}')} \mathrm{d}k\right].$$
(2.10)

Through the introduction of the atomic scattering factor  $f_l(\mathbf{k}, \mathbf{k}_{\ell})$  we have managed to eliminate the integral over d**r**. What remains is the integral over dk which still practically excludes calculations of holograms for large system of atoms. To bypass this integral we approximate the atomic scattering factor with  $f_l(\mathbf{k}, \mathbf{k}) \approx f_l(\bar{k}\hat{\mathbf{k}}, \bar{k}\hat{\mathbf{k}}_{\ell})$ , where  $\bar{k}$  is a characteristic value of  $N_i$  (e.g., the mode). Now we can rewrite (2.10) as (Dul & Korecki 2012)

$$\bar{\chi}_i(\hat{\mathbf{k}}) = -2r_{\rm e} \sum_l \frac{f_l(\bar{k}\hat{\mathbf{k}}, \bar{k}\hat{\mathbf{k}}_\ell)}{|\mathbf{R}_i - \mathbf{r}'_\ell|} h_i(\vartheta, |\mathbf{R}_i - \mathbf{r}'_\ell|).$$
(2.11)

where  $\vartheta = \arccos[-\hat{\mathbf{k}} \cdot (\mathbf{R}_i - \mathbf{r}'_{\ell})/|\mathbf{R}_i - \mathbf{r}'_{\ell}|]$ . Equation (2.11) can be conveniently used to generate white beam holograms for large atomic clusters provided that the dk integral in  $h_i$  can be evaluated.

## 2.2 The effective spectrum and its approximation

To find a compact expression for  $h_i$  it is essential to specify the shape of  $N_i$ . Put simply,  $h_i$  is given by the Fourier transform of  $N_i$ . This can be easily seen if we treat  $|\mathbf{R}_i - \mathbf{r'}|(1 - \cos \vartheta')$  as a single variable in equation (2.9). This actually tells us a lot about the expected shape of white beam

<sup>&</sup>lt;sup>2</sup>To get equation (2.9) we have rewritten the exponent in equation (2.7) as  $e^{ik|\mathbf{R}_i - \mathbf{r}|(1 + \cos \vartheta'')}$ , where  $\vartheta'' = \arccos[\hat{\mathbf{k}} \cdot (\mathbf{R}_i - \mathbf{r})/|\mathbf{R}_i - \mathbf{r}|]$ , and replaced  $1 + \cos \vartheta''$  with  $1 - \cos \vartheta'$ . In doing so we have used  $\cos \vartheta'' = -\cos(\pi - \vartheta'')$  and  $\vartheta' = \pi - \vartheta''$ .

holograms. If  $N_i$  is highly localized then the hologram will extend to the whole sphere. This is the case of monochromatic radiation where  $N_i$  can be approximated by a Dirac delta that is located at some value  $k_0$ , i.e.,  $N_i(k) = \delta(k - k_0)$ . In figures 1.2(c) and 1.2(d) the interference fringes encompass the whole sphere. For a broadband energy spectrum  $\bar{\chi}_i$  will be localized around  $\mathbf{R}_i - \mathbf{r}'$ , i.e., around the forward scattering direction. The interference fringes should be in close vicinity of this direction. These conclusions follow from the Fourier transform of 1, namely  $\int_{-\infty}^{\infty} e^{ikx} dk/\sqrt{2\pi} = 2\pi\delta(x)$ .

Example incident spectra  $(I_0)$  are presented in figure 2.1(top row). The spectra were simulated with the XOP package (del Río & Dejus 2004) for the I12 beamline at the Diamond Light Source (http://www.diamond.ac.uk/Beamlines.html) and for the P61.1 beamline at Petra III (DESY 2011, 2014). A 2 mm Cu absorber was assumed for I12 and a 10 mm Cu absorber was assumed for P61.1. The I12 and P61.1 beam lines utilize wigglers. X-ray spectra, analogous to those shown in figure 2.1(top row), can be also obtained from bending magnet beam lines.

Effective spectra  $N_i$  which were obtained from the incident I12 and P61.1 spectra are presented in figure 2.1(bottom row). The effective spectra were calculated for gallium atoms (K edge at 10.37 keV), i.e., by multiplying  $I_0$  by  $\sigma_{\text{Ga}}^0$ . The fact that we have used a specific example of gallium and only gallium might raise concerns to the generality of the discussion that follows. However, for energies far above the K edge, the shape of the spectra is approximately the same for different elements. To show this we consider two elements *i* and *j* and the ratio of their effective spectra  $N_i/N_j$ . For energies far above the K edge the photoionisation cross section  $\sigma_i^0$  (similarly  $\sigma_j^0$ ) can be approximated by the Victoreen equation (Victoreen 1943, 1948, 1949)

$$\sigma_i^0 = \frac{a_i}{E^3} + \frac{b_i}{E^4},$$
(2.12)

where  $a_i$  and  $b_i$  are constants. Now from the limit

$$\lim_{E \to \infty} \frac{N_i}{N_j} = \lim_{E \to \infty} \frac{\sigma_i}{\sigma_j} = \frac{a_i}{a_j}$$
(2.13)

it follows that

$$N_i = a_i N_j / a_j \tag{2.14}$$

which implies that for high energies the shape of  $N_i$  is approximately independent of the *i* element and only its amplitude changes. Equation (2.14) is only valid for incident energy spectra which have a lower cutoff far above the K edges of element *i* and *j*. For realistic spectra produced by currently available hard x-ray wigglers this result is only approximate, yet guaranties that our discussion does not lose generality.

In order to qualitatively describe  $N_i$  one has to provide some parameters which will describe its shape. The first such approach was proposed by Korecki et al. (2006*a*) where the Lorentz distribution



Figure 2.1: Example incident  $(I_0)$  and effective energy spectra  $(N_i)$  for the I12 beam line at Diamond and the P61.1 beam line at Petra III. The effective spectra are calculated for gallium (i = Ga) and fitted with Lorentz (dashed line) and Gumbel (solid line) functions. The areas under the dotted graphs are normalized to unity. The values of the fits are: for I12  $k_0 = 36.1 \text{ Å}^{-1}$ ,  $\Delta k = 15.8 \text{ Å}^{-1}$ ,  $\mu_0 = 34.7 \text{ Å}^{-1}$ ,  $\Delta \mu = 7.8 \text{ Å}^{-1}$ , and for P61.1  $k_0 = 60.9 \text{ Å}^{-1}$ ,  $\Delta k = 26.1 \text{ Å}^{-1}$ ,  $\mu_0 = 58.4 \text{ Å}^{-1}$ ,  $\Delta \mu = 12.9 \text{ Å}^{-1}$ .

(also known as the Cauchy-Lorentz distribution) was used to describe  $N_i$ . The Lorentz distribution is defined as

$$N_{\rm L}(k) = \frac{1}{2\pi} \frac{\Delta k}{(k - k_0)^2 + (\Delta k/2)^2},$$
(2.15)

where  $k_0$  gives the position of its center and  $\Delta k$  is the full width at half maximum (FWHM). In figure 2.1(bottom row) the Lorentz function is fitted to the effective spectra. Although the agreement between the shape of the effective spectra and the Lorentz fits is far from perfect the usage of the Lorentz function has its advantages. Many useful analytic results can be obtained with it especially when applied to structure retrieval procedures (Korecki et al. 2006*a*, Korecki, Novikov & Tolkiehn 2009). We will encounter the usefulness of the Lorentz approximation of  $N_i$  when we apply the wavelet transform to white beam XFH. At this point we make the small angle approximation

$$1 - \cos\vartheta' \approx \frac{(\vartheta')^2}{2} \tag{2.16}$$

which is justified since, as already mentioned, for a broadband effective spectrum  $h_i$  is localized around the  $\mathbf{R}_i - \mathbf{r}$  direction. With the small angle approximation and  $N_{\rm L}$  equation (2.9) can be evaluated to (Korecki, Novikov & Tolkiehn 2009)

$$h_{\rm L}\left(\vartheta', |\mathbf{R}_i - \mathbf{r}|\right) = e^{-\beta q(\vartheta')^2} \cos\left[q(\vartheta')^2\right],\tag{2.17}$$

where

$$\beta = \frac{\Delta k}{2k_0} \quad \text{and} \quad q = \frac{k_0 |\mathbf{R}_i - \mathbf{r}|}{2}.$$
(2.18)

Apart from the Lorentz function, the effective spectrum  $N_i$  can be also approximated with the Gumbel distribution [a type of an extreme value distribution (Coles 2001)], i. e.,

$$N_{\rm G}(k) = \frac{1}{\Delta\mu} \exp\left[-\frac{k-\mu_0}{\Delta\mu} - \exp\left(-\frac{k-\mu_0}{\Delta\mu}\right)\right],\tag{2.19}$$

where  $\mu_0$  is its mode and  $\Delta\mu$  determines its spread. The Gumbel distribution is fitted to the effective spectra in figure 2.1(bottom row). In comparison with the Lorentz function the Gumbel takes into account the heavily skewed nature of the effective spectra. It reflects the shape of the effective spectra very well, far better then the Lorentz distribution. For the Gumbel distribution  $h_i$  is equal to (Dul & Korecki 2012)

$$h_G\left(\vartheta', |\mathbf{R}_i - \mathbf{r}|\right) = \operatorname{Re}\left[e^{i\mu_0|\mathbf{R}_i - \mathbf{r}|(\vartheta')^2}\Gamma\left(1 - i\Delta\mu|\mathbf{R}_i - \mathbf{r}|(\vartheta')^2/2\right)\right],\tag{2.20}$$

where  $\Gamma$  is the gamma function (Olver et al. 2010).

Although, expressions (2.17) and (2.20) together with (2.11) are only approximate, they can be used to calculate white beam holograms for comparison with experiment.



Figure 2.2: White beam hologram for an absorber - point scatterer system. The point scatterer is located along the z axis 3.19 Å from the absorber. (a) A white beam hologram calculated with equation (2.8). The integral over dk in  $h_i$  was calculated numerically. The I12 energy spectrum from figure 2.1(bottom row) was used for the integration. The absorber was assumed to be a gallium atom (i = Ga). (b) Profiles of  $\bar{\chi}_{\text{Ga},\delta}$  along  $\theta$  for the numeric calculation (dots) from (a) and for Lorentzian  $h_{\text{L}}$  (dashed line) and Gumbel  $h_{\text{G}}$  (solid line) approximations of the effective spectrum.



Figure 2.3: Profiles of white beam holograms generated for two atom systems with Ga as the absorbing atom and N (a) and Ga (b) scatterers. The scatterers are located along the z axis 3.19 Å from the absorbed. The dashed lines represent calculations with equation (2.10) whereas the solid ones represent calculations with equation (2.11) and  $h_G$ .

We would now like to compare the holograms obtained with  $h_L$ ,  $h_G$  and those obtained by a direct integration over dk. Consider first a point scattering object which is located at  $\mathbf{r}'$ . This is equivalent to putting  $\rho(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}')$  in (2.8). If we place the detector at the origin  $\mathbf{R}_i = (0, 0, 0)$  then  $\bar{\chi}_i$  is equal to

$$\bar{\chi}_{i,\delta}(\hat{\mathbf{k}}) = -\frac{2r_{\mathbf{e}}}{r'}h_i(\vartheta, r'), \qquad (2.21)$$

where  $r' = |\mathbf{r}'|$  and  $h_i$  can be calculated by a direct numerical integration of equation (2.9) or we can use either  $h_L$  or  $h_G$ .

An example  $\bar{\chi}_{i,\delta}$  hologram is presented in figure 2.2(a). The calculation was preformed for a scatterer which was located along the z axis 3.19Å from the absorber  $[\mathbf{r}' = (0, 0, 3.19Å)]$ . The hologram was obtained by a direct numerical integration of  $h_i$  over dk. The Diamond I12 spectrum was used for the integration and the absorbing atom was assumed to be a gallium atom (i = Ga). A profile of the hologram along  $\theta$  is shown in figure 2.2(b) together with profiles of  $\bar{\chi}_{i,\delta}$  calculated with  $h_L$  and  $h_G$ . The necessary values of  $k_0$ ,  $\Delta k$ ,  $\mu_0$  and  $\Delta \mu$  were taken from the fits to  $N_{\text{Ga}}$  [figure 2.1(bottom left corner)].

The most eye catching feature of figure 2.2(b) is the nearly perfect agreement between  $\bar{\chi}_{\text{Ga},\delta}$  obtained from the direct numerical integration over dk and  $h_G$ . On the other hand, the agreement between these two results and the one obtained with  $h_L$  is only moderate. The holograms are, as anticipated earlier, localized around the forward scattering direction, i.e.,  $\mathbf{r}'$ .

Apart from the effective spectrum approximation we have also assumed in (2.11) that the atomic form factor  $f_l(\mathbf{k}, \mathbf{k}_{\ell})$  can be approximated by  $f_l(\bar{k}\hat{\mathbf{k}}, \bar{k}\hat{\mathbf{k}}_{\ell})$ . To show that this is in fact a good approximation we perform calculations for two systems of atoms. The first system consists of a gallium absorber and a nitrogen scatterer. In the second system the nitrogen scatterer is replaced with a gallium atom. As before the scatterers are localized at  $\mathbf{r}' = (0, 0, 3.19\text{Å})$ . For the Gumbel approximation of  $N_i$  we put  $\bar{k} = \mu_0 = 34.7 \text{ Å}^{-1}$ . Figure 2.3 shows profiles of the obtained holograms. The profiles have been obtained with equations (2.10) [before the approximation of  $f_l(\mathbf{k}, \mathbf{k}_{\ell})$  and equation (2.11) [after the approximation of  $f_l(\mathbf{k}, \mathbf{k}_{\ell})$ ]. The exact and approximate results are in good agreement and justify the approximations.

The conclusion that can be drawn from this short part is that white beam x-ray fluorescence holograms are, to a large extent, determined by the shape of the effective spectra  $N_i$ . Although these spectra can be precisely described with programs used for modeling of x-ray sources (del Río & Dejus 2004), such an approach is impractical in white beam XFH. The need for a simple and compact analytic expression for  $\bar{\chi}_i$  has lead to the approximation of the effective spectra with Lorentz and Gumbel distributions. Both of these approximations provide useful formulas which can be used in practice, with Gumbel giving more accurate results. Moreover, the Gumbel distribution can also be used to accurately describe x-ray spectra from x-ray tubes, as shown by Dabrowski et al. (2013).

## 2.3 FROM WHITE BEAM HOLOGRAMS TO WAVELETS

One of the main problems that we consider in this work is structure retrieval from white beam holograms. In this endeavour we concentrate on the wavelet analysis of white beam holograms. The approach is based on the observation that the white beam holographic signal has the same properties as wavelets (Korecki, Novikov & Tolkiehn 2009). To show the connection between wavelets and white beam holograms we first define the wavelet transform in one dimension closely following the work of Mallat (2008). Then we introduce the continuous spherical wavelet transform as proposed by Antoine & Vandergheynst (1999) and Antoine et al. (2002) and apply it to the analysis of white beam holograms. We consider only continuous wavelet transforms.

#### 2.3.1 WAVELETS IN 1D

Simply speaking a wavelet, or more precisely a mother wavelet, is a square-integrable function  $\psi(t) \in \mathbf{L}^2(\mathbb{R})$  that is normalized to unity, centered around t = 0 and fulfills the zero mean condition

$$\int_{-\infty}^{\infty} \psi(t) \mathrm{d}t = 0. \tag{2.22}$$

Once the mother wavelet is defined it can be used to generate a wavelet family or simply a collection of new wavelets. A member  $\psi_{u,s}(t)$  of the wavelet family is obtained by scaling the mother wavelet by s > 0 and translating it by  $u \in \mathbb{R}$ 

$$\psi_{u,s}(t) = \frac{1}{\sqrt{s}}\psi\left(\frac{t-u}{s}\right).$$
(2.23)

The s parameter is sometimes referred to as the scale. If s < 1 then the wavelet is compressed, its frequency becomes larger. If s > 1 the wavelet is stretched, its frequency becomes smaller.

Two popular examples of functions that satisfy the conditions for a wavelet are the *Mexican hat* wavelet and the Morlet wavelet. The *Mexican hat* wavelet is defined as (Mallat 2008)

$$\psi(t) = \frac{2}{\pi^{1/4}\sqrt{3\sigma}} \left(\frac{t^2}{\sigma^2} - 1\right) \exp\left(-\frac{t^2}{2\sigma^2}\right),\tag{2.24}$$

where  $\sigma > 0$ . The Morlet wavelet is defined as (Amir-Homayoon 2012)

$$\psi(t) = a \left( e^{i\omega_0 t} - e^{-\omega_0^2/2} \right) e^{-t^2/2}, \qquad (2.25)$$

where  $a = \pi^{-1/4} \left( 1 - 2e^{-3\omega_0^2/4} + e^{-\omega_0^2} \right)^{-1/2}$  and  $\omega_0 > 0$ . These two wavelets and their scaled and translated versions are plotted in figure 2.4.

With the wavelet family in place the wavelet transform  $\tilde{f}(s, u)$  of a function f(t) can be defined as (Mallat 2008)

$$\widetilde{f}(s,u) = \int_{-\infty}^{\infty} f(t) \frac{1}{\sqrt{s}} \psi^*\left(\frac{t-u}{s}\right) \mathrm{d}t.$$
(2.26)



Figure 2.4: Example wavelets. (a) The scaled and translated *Mexican hat* wavelet for  $\sigma = 1$ . (b) The real part of the scaled and translated Morlet wavelet for  $\omega_0 = 1$ .

Please note that the integral above transforms a function of one variable into a function of two variables.  $\tilde{f}(s, u)$  can be also written as a cross-correlation<sup>3</sup>  $\tilde{f}(s, u) = f \star \bar{\psi}_s$ , where  $\bar{\psi}_s(t) = \psi^*(t/s)/\sqrt{s}$ . Expressing  $\tilde{f}(s, u)$  as a correlation is the basis of many practical applications. It is also the main idea behind the application of wavelets to white beam holograms.

An important property of the wavelet transform is its invertibility. The original signal f(t) can be recovered from  $\tilde{f}(s, u)$  if the mother wavelet  $\psi(t)$  satisfies

$$0 < C_{\psi} = \int_0^\infty \frac{|\hat{\psi}(\omega)|^2}{\omega} \mathrm{d}\omega < \infty, \qquad (2.27)$$

where  $\hat{\psi}(\omega)$  is the Fourier transform of  $\psi(t)$ . Equation (2.27) is known as the *admissibility condition* and plays an important role in the theory of wavelets. The inversion of  $\tilde{f}(s, u)$  is given by

$$f(t) = \frac{1}{C_{\psi}} \int_0^{\infty} \int_{-\infty}^{\infty} \widetilde{f}(s, u) \frac{1}{\sqrt{s}} \psi\left(\frac{t-u}{s}\right) \mathrm{d}u \frac{\mathrm{d}s}{s^2}.$$
 (2.28)

The integral over ds in (2.28) can be also performed in a limited range of scales, from some  $s_b$  to some  $s_c$ . In this case the recovered signal f(t) will contain the frequency components that correspond to the scales in the range from  $s_b$  to  $s_c$ . Frequency components that will correspond to scales outside of this range will be strongly suppressed.

As a final remark we would like to point out that for non-orthogonal wavelets other inversion formulas are possible. This it due to the redundancy of  $\tilde{f}(s, u)$  which contains much more information than needed. For example an inversion formula for f(t) can read (Farge 1992)

$$f(t) = \frac{1}{C_{\delta}} \int_0^\infty \widetilde{f}(s,t) \frac{\mathrm{d}s}{s^{3/2}},\tag{2.29}$$

<sup>&</sup>lt;sup>3</sup>The cross-correlation of two functions f(t) and g(t) is defined as  $f \star g = \int_{-\infty}^{\infty} f^*(\tau)g(t+\tau)d\tau = \int_{-\infty}^{\infty} f^*(\tau-t)g(\tau)d\tau$ .

where  $C_{\delta} = (2\pi)^{1/2} \int_{-\infty}^{\infty} \hat{\psi}(\omega) \frac{d\omega}{\omega}$ . Equation (2.29) corresponds to putting a Dirac delta function in place of  $\psi((t-u)/s)/\sqrt{s}$  in (2.28).

### 2.3.2 The Heisenberg box

The wavelet transform decomposes the signal given by f(t) in the basis of scaled and translated wavelets  $\psi_{u,s}(t)$ . There are a number of mother wavelets which can be used to compute (2.26), the *Mexican hat* and Morlet wavelets being just two particular examples. In general, the choice of a given wavelet family depends on the considered problem.

The main reason why one would prefer to decompose a function (e.g., a time series or an image) into wavelets rather than for example sines and cosines is that wavelets are localized in both space and in the frequency domain whereas sine and cosine functions are only localized in the frequency domain. To give this more meaning consider a scaled and translated wavelet  $\psi_{u,s}(t)$ . This wavelet is centered at u and has a variance of

$$\int_{-\infty}^{\infty} (t-u)^2 |\psi_{u,s}(t)|^2 \mathrm{d}t = s^2 \int_{-\infty}^{\infty} t^2 |\psi(t)|^2 \mathrm{d}t = s^2 \sigma_t^2.$$
(2.30)

In the frequency domain  $\hat{\psi}_{u,s}(\omega)$  is centered around  $\eta/s = \int_{-\infty}^{\infty} \omega |\hat{\psi}_{u,s}(\omega)|^2 d\omega$  and has a variance of

$$\int_{-\infty}^{\infty} \left(\omega - \frac{\eta}{s}\right)^2 |\hat{\psi}_{u,s}(\omega)|^2 \mathrm{d}\omega = \frac{1}{s^2} \int_{-\infty}^{\infty} \left(\omega - \eta\right)^2 |\hat{\psi}(\omega)|^2 \mathrm{d}\omega = \frac{\sigma_{\omega}^2}{s^2}.$$
 (2.31)

The location of the wavelet can be thus parameterized in the  $t - \omega$  plane with four numbers. The wavelet is centered at  $(u, \eta/s)$  and its spread is given by a box with dimensions  $(s \sigma_t) \times (\sigma_{\omega}/s)$ . Schematically this is shown in figure 2.5 for two wavelets  $\psi_{u_1,s_1}(t)$  and  $\psi_{u_2,s_2}(t)$ . The area of the box is constant  $\sigma_t \sigma_{\omega}$ . It does not depend on the scale nor on the location of the wavelet on the plane. This description of the localization of wavelets is a type of uncertainty principle, like the Heisenberg's uncertainty principle in quantum mechanics. If the area of the boxes in figure 2.5 is constant then we neither can precisely define the frequency nor the positions in t. If, despite this, we try, we will lose information about one of the two. An example of such a wave is the classic sine wave for which  $\sigma_{\omega} = 0$  and  $\sigma_t = \infty$ . The frequency is precisely defined but the positions is completely undetermined.

Owing to their localization in space and in the frequency domain wavelets are a natural choice when it comes to the analysis of various signals that occur in nature and everyday life. If someone blows a whistle then that signal is localized somewhere in time. If that person blows the whistle a few more times in such a way that the duration of periods between each blow and the blows themselves are not equal in time, then the signal has many local features and is non-stationary, i.e., its frequency content changes in time. Such signals are actually ubiquitous and the wavelet transform is perfectly suited for their analysis.



Figure 2.5: The uncertainty principle for wavelets. The figure is analogical to Fig. 4.9 in (Mallat 2008).



Figure 2.6: Properties of the white beam holographic signal. The right plot is a profile plot along the orange dashed, full circle visible in the left plot. The patterns are generated for point scattering objects but analogical plots can be obtained for atoms. The figure is analogical to the one in (Korecki, Novikov & Tolkiehn 2009). The figure is not to scale. The 1/r' term in  $\bar{\chi}_{i,\delta}$  was omitted.

## 2.3.3 The continuous spherical wavelet transform

Consider the system as shown in figure 2.6(a) together with the corresponding white beam hologram. A profile of the hologram along the full dashed circle is shown in figure 2.6(b). Apart from the absorbing atom there are four point scatterers in the system. Each scatterer is placed at a different distance from the absorber. We would like to determine the positions of the four scatterers with respect to the absorbing atom. Simply speaking, from figure 2.6, we can conclude that the distance of a scatterer from the absorber is related to the spread of its holographic signal. The spread can be in this case defined as  $\Delta \omega$ . The scatterer with the largest spread is closest to the absorbing atom whereas the scatterer with the lowest spread is most distant from the absorber. The distances and spreads of the remaining two scatterers lie in-between. This behavior follows from equation (2.21). If the scatterer is placed at  $\mathbf{r}'$  then the spread of the hologram, according to  $h_L$ , is determined by  $q = k_0 r'/2$  and decreases when the absorber-scatterer distance r' increases. The direction in which a given scatterer is located is determined by the placement of the scatterer's holographic signal on the sphere and is given by the unit vector  $\hat{\mathbf{r}}'$ . Thus, the placement of the holographic signal on the sphere and its spread uniquely determine the position of a scatterer with respect to the absorber.

The holographic signals plotted in figure 2.6 bear a striking resemblance to wavelets which we have defined earlier. Take for example the holographic signal of the scatterer at 2.5 Å which we will denote by  $\chi_{2.5}$ . The holographic signal from the scatterer at 10 Å can be obtained from  $\chi_{2.5}$  if  $\chi_{2.5}$  is compressed (squeezed) and rotated on the sphere to the appropriate position. Similarly holographic signals from the scatterers at 25 Å and 50 Å can be obtained from  $\chi_{2.5}$  if  $\chi_{2.5}$  is appropriately compressed and rotated. The squeezing and rotation of the holographic signal is analogous to scaling and translation of the mother wavelet  $\psi(t)$ . It seems natural to apply the wavelet transform to the analysis of white beam holographic data. To do so we need to define the continuous wavelet transform on a 2D sphere.

The mother wavelet on a unit sphere is defined as a square-integrable function  $\psi(\theta, \phi) \in \mathbf{L}^2(S^2)$  that is localized around the north pole. The wavelet family is generated through rotations and scaling of the mother wavelet.

On a sphere the definition of scaling is not straightforward since the sphere is a closed surface. It is compact and does not have boundaries. The scaling operation on a sphere is defined through a correspondence between wavelets on a plane and wavelets on a sphere (Antoine & Vandergheynst 1999, Wiaux et al. 2005). This correspondence is based on the stereographic projection. In the stereographic projection a point  $(\theta, \phi)$  on the sphere is projected into a point  $(\varrho, \phi)$  on the plane (see figure 2.7), where  $\varrho = 2 \tan \theta/2$ . The plane is tangent to the sphere at the north pole and the point  $(\varrho, \phi)$  is given in polar coordinates. Through the stereographic projection one defines a unitary operator  $\Pi$  which transform a wavelet on a sphere into a wavelet on the tangent plane. The action of  $\Pi$  on  $\psi(\theta, \phi)$  is given by (Wiaux et al. 2005)

$$\Pi\psi(\theta,\phi) = \left(1 + \frac{\varrho^2}{4}\right)^{-1}\psi\left(2\arctan\frac{\varrho}{2},\phi\right) = \psi(\varrho,\phi)$$
(2.32)

and its inverse  $\Pi^{-1}$  as

$$\Pi^{-1}\psi(\varrho,\phi) = \left(1 + \tan^2\frac{\theta}{2}\right)\psi\left(2\tan\frac{\theta}{2},\phi\right) = \psi(\theta,\phi).$$
(2.33)

Under the action of  $\Pi$ ,  $\psi(\theta, \phi)$  is admissible and square-integrable on the sphere, whereas  $\psi(\varrho, \phi)$  is admissible and square-integrable on the tangent plane. The scaling is accomplished by projecting the mother wavelet onto the tangent plane ( $\Pi$ ), scaling the wavelet on the plane and then projecting the wavelet back ( $\Pi^{-1}$ ) onto the sphere. The lifting of the wavelet from the sphere onto the plane can be represented as

$$\psi_s(\theta, \phi) = \frac{2s}{(s^2 - 1)\cos\theta + (s^2 + 1)}\psi(\theta_s, \phi),$$
(2.34)

where  $\tan(\theta_s/2) = s^{-1} \tan(\theta/2)$ .

The rotation of the mother wavelet from the north pole to a point  $\hat{\mathbf{k}}_0 = (\theta_0, \phi_0)$  on the sphere can be represented through three Euler angels  $(\phi_0, \theta_0, \gamma_0)$ . This rotation is defined by an operator  $\mathcal{R}_{\phi_0,\theta_0,\gamma_0}$  which can be decomposed to  $\mathcal{R}_{\phi_0,\theta_0,\gamma_0} = \mathcal{R}_{\phi_0}^{\hat{\mathbf{z}}} \mathcal{R}_{\theta_0}^{\hat{\mathbf{y}}} \mathcal{R}_{\gamma_0}^{\hat{\mathbf{z}}}$ , where  $\mathcal{R}_{\theta_0}^{\hat{\mathbf{y}}}$  is a rotation operator around the y axis by  $\theta_0$  (analogously for the z axis and the  $\phi_0$  and  $\gamma_0$  angels).  $\mathcal{R}_{\phi_0,\theta_0,\gamma_0}$  can be expressed as  $\mathcal{R}_{\phi_0,\theta_0,\gamma_0} = \mathcal{R}_{\hat{\mathbf{k}}_0} \mathcal{R}_{\gamma_0}^{\hat{\mathbf{z}}} = \mathcal{R}_{\hat{\mathbf{k}}_0,\gamma_0}$ , where  $\mathcal{R}_{\hat{\mathbf{k}}_0} = \mathcal{R}_{\phi_0}^{\hat{\mathbf{z}}} \mathcal{R}_{\theta_0}^{\hat{\mathbf{y}}}$ . The  $\mathcal{R}_{\gamma_0}^{\hat{\mathbf{z}}}$  operator rotates the mother wavelet around the north pole by  $\gamma_0$  and  $\mathcal{R}_{\hat{\mathbf{k}}_0}$  takes it to  $\hat{\mathbf{k}}_0$ . If  $\hat{\mathbf{k}} = (\theta, \phi)$  denotes an arbitrary point on the sphere then the rotation is accomplished by

$$\mathcal{R}_{\hat{\mathbf{k}}_{0},\gamma_{0}}\psi_{s}(\hat{\mathbf{k}}) = \psi_{s}\left(\mathcal{R}_{\hat{\mathbf{k}}_{0},\gamma_{0}}^{-1}\hat{\mathbf{k}}\right) = \psi_{\hat{\mathbf{k}}_{0},\gamma_{0},s}(\hat{\mathbf{k}}).$$
(2.35)

where  $\mathcal{R}_{\hat{\mathbf{k}}_0,\gamma_0}^{-1}$  is the inverse of  $\mathcal{R}_{\hat{\mathbf{k}}_0,\gamma_0}$ .  $\psi_{\hat{\mathbf{k}}_0,\gamma_0,s}(\hat{\mathbf{k}})$  is a scaled and rotated wavelet on a sphere which can be used to define the continuous wavelet transform on a sphere.

The continuous spherical wavelet transform (CSWT) of a function  $f(\hat{\mathbf{k}})$  on a sphere is defined as (Antoine et al. 2002, Antoine & Vandergheynst 1999)

$$\widetilde{f}(\widehat{\mathbf{k}}_{0},\gamma_{0},s) = \int_{S^{2}} \psi^{*}_{\widehat{\mathbf{k}}_{0},\gamma_{0},s}(\widehat{\mathbf{k}})f(\widehat{\mathbf{k}})\mathrm{d}\Omega, \qquad (2.36)$$

where the integration is over the surface of the sphere. For the transform to be invertible the mother wavelet must satisfy the admissibility condition which for wavelets on a sphere reads

$$0 < C_{\psi}^{l} = \frac{8\pi^{2}}{2l+1} \sum_{|m| \leq l} \int_{0}^{\infty} \left| (\hat{\psi}_{s})_{l,m} \right|^{2} \frac{\mathrm{d}a}{a^{3}} < \infty,$$
(2.37)



Figure 2.7: The stereographic projection of a sphere onto a plane tangent at the north pole. A point  $(\theta, \phi)$  on the sphere is mapped into a point  $(\varrho, \phi)$  on the plane, where  $\varrho = 2 \tan \theta/2$ . On the plane  $\varrho$  and  $\phi$  are polar coordinates and  $x = \varrho \sin \phi$ ,  $y = \varrho \cos \phi$ . The  $\Pi$  and  $\Pi^{-1}$  operators establish a correspondence between wavelets on a sphere and on the plane. Figure adopted from Wiaux et al. (2005).

where  $(\hat{\psi}_s)_{l,m} = \int_{S^2} Y_{l,m}^*(\hat{\mathbf{k}}) \psi_s(\hat{\mathbf{k}}) d\Omega$  and  $Y_{l,m}^*(\hat{\mathbf{k}})$  are the complex conjugate of spherical harmonics. For wavelets on a sphere the admissibility condition is equivalent to the zero mean condition

$$\int_{S^2} \frac{\psi(\theta, \phi)}{1 + \cos\theta} d\Omega = 0$$
(2.38)

which is much easier to use in practice. When (2.38) is satisfied  $\tilde{f}(\hat{\mathbf{k}}_0, \gamma_0, s)$  can be inverted through

$$f(\hat{\mathbf{k}}) = \int_0^{2\pi} \int_0^\infty \int_{S^2} \tilde{f}(\hat{\mathbf{k}}_0, \gamma_0, s) \left[ \mathcal{R}_{\hat{\mathbf{k}}_0, \gamma_0} \mathcal{L}_{\Psi} \psi_s(\hat{\mathbf{k}}) \right] d\Omega_0 \, \frac{\mathrm{d}s}{s^2} \, \mathrm{d}\gamma_0, \tag{2.39}$$

where the action of the  $\mathcal{L}_{\Psi}$  operator is defined in the Fourier space as  $\mathcal{L}_{\Psi}(\hat{\psi}_s)_{l,m} = (\hat{\psi}_s)_{l,m}/C_{\psi}^l$ .

#### CHOOSING A PARTICULAR MOTHER WAVELET

In order to apply the continuous spherical wavelet transform to white beam XFH we have to specify the mother wavelet. Since the wavelet transform can be viewed as a correlation between the analyzed signal and specially prepared wavelets we chose the mother wavelet in such a way that it resembles the white beam holographic signal of a point scatterer as close as possible. Owing to such a choice of the mother wavelet we will be able to interpret the wavelet transform space as a real space image of the local structure around the absorbing atoms.

There are two important properties of the mother wavelet which follow from the properties of the white beam holographic signal. Firstly, since the holographic signal is invariant under rotations around  $\mathbf{R}_i - \mathbf{r}'$  we require the mother wavelet to be invariant under rotations around the north pole. In other words the mother wavelet should be isotropic  $\psi(\hat{\mathbf{k}}) = \psi(\theta)$ . Secondly, from figure 2.6 we have concluded that the holographic signal has the largest spread  $\Delta \omega$  for atoms that are closest to the absorber. Holographic signals for all other atoms have a smaller value of  $\Delta \omega$ . This implies that the mother wavelet can be constructed in such a way that it will only require compression. The scale range can be limited to  $s \leq 1$ . The mother wavelet should be as broad as possible. The maximal spread of the mother wavelet can be determined with the small angle approximation (2.16). The mother wavelet can not be broader then the holographic signal for which (2.16) holds.

The rotational invariance of the mother wavelet, the limited range of scales together with the requirement of the small angle approximation simplify the calculation of the wavelet transform. With the small angle approximation (2.16) the scaling operation (2.34) can be written as

$$\psi_s(\theta) = \frac{1}{s}\psi(\theta_s),\tag{2.40}$$

where  $\theta_s = \theta/s$ . An isotropic mother wavelet is immune to the action of  $\mathcal{R}^{\hat{z}}_{\gamma_0}$  and the rotation of the wavelet reduces itself to

$$\mathcal{R}_{\hat{\mathbf{k}}_{0}}\psi_{s}(\hat{\mathbf{k}}) = \psi_{s}\left(\mathcal{R}_{\hat{\mathbf{k}}_{0}}^{-1}\hat{\mathbf{k}}\right) = \psi_{\hat{\mathbf{k}}_{0},s}(\hat{\mathbf{k}}), \qquad (2.41)$$

where  $\mathcal{R}_{\hat{\mathbf{k}}_0}^{-1}$  is the inverse of  $\mathcal{R}_{\hat{\mathbf{k}}_0}$ . For a white beam hologram and the described mother wavelet the continuous spherical wavelet transform (2.36) can be written as

$$\widetilde{\chi}_i(\hat{\mathbf{k}}_0, s) = \int_{S^2} \bar{\chi}_i(\hat{\mathbf{k}}) \psi_{\hat{\mathbf{k}}_0, s}(\hat{\mathbf{k}}) \mathrm{d}\Omega.$$
(2.42)

The zero mean condition simplifies to

$$\int_0^\infty \psi(\theta) \ \theta \mathrm{d}\theta = 0, \tag{2.43}$$

where we have replaced the integration range  $(0, \pi)$  with  $(0, \infty)$ . This replacement is justified for highly localized wavelets since away from the north pole the amplitude of the wavelet is zero. For small scales the inverse can be evaluated with (Antoine & Vandergheynst 1999, Farge 1992)

$$\bar{\chi}_i(\hat{\mathbf{k}}) = \frac{1}{C_\delta} \int_0^\infty \tilde{\chi}_i(\hat{\mathbf{k}}, s) \frac{\mathrm{d}s}{s^2},\tag{2.44}$$

where we have assumed that  $\psi_{\hat{\mathbf{k}}_0,s}(\hat{\mathbf{k}})$  are not orthogonal. The  $C_{\delta}$  constant is given by

$$C_{\delta} = 2\pi \int_{0}^{\infty} \hat{\psi}(\omega) \frac{\mathrm{d}\omega}{\omega}$$
(2.45)

where  $\hat{\psi}(\omega) = \int_0^{2\pi} \int_0^\infty \psi(\theta) e^{-i\omega \cos \theta} \theta d\theta d\phi / (4\pi^2).$ 

For the remainder of the text we will be using the following scaled mother wavelet which was proposed by Korecki, Novikov & Tolkiehn (2009)

$$\psi_s(\theta) = -\frac{1}{s} \exp(-\beta q_0 \theta^2 / s^2) \left[ \cos\left(\frac{q_0 \theta^2}{s^2}\right) - \beta \sin\left(\frac{q_0 \theta^2}{s^2}\right) \right], \qquad (2.46)$$

where  $q_0 = k_0 r_0/2$ ,  $\beta = \Delta k/(2k_0)$ , the scale parameter s is equal to  $s = (r/r_0)^{-1/2}$  and  $r \ge r_0$ . The definition of the scale parameter connects the distance from the absorber r with s. It ensures that the scale parameter will be smaller or equal then one. The  $r_0$  parameter has the dimension of length and is set to the smallest possible value for which the small angle approximation (2.16) holds.

A graphical comparison of  $\psi_s$  with  $h_L$  and  $h_G$  for the hologram from figure 2.2(b) is given in figure 2.8(a). The shape of the wavelet, given by (2.46), should resemble the shape of the holographic signal as close as possible. It nearly matches the shape of the holographic signal given by  $h_L$ . Actually  $\psi_s$  reduces to  $h_L$  when  $\beta \to 0$ . The wavelet's shape is also closely resembled by  $h_G$ . Throughout the  $\theta$  range  $h_L$  and  $h_G$  are slightly out of phase with  $\psi_s$ . Here a question arises. What  $k_0$  and  $\Delta k$  values one should use when one applies  $\psi_s$  to the analysis of white beam holograms? The most simple choice is to use the values from the Lorentz fit in figure 2.1(bottom row). These were used to plot  $\psi_s$  in figure 2.8(a). One can, however, try to adjust the  $k_0$  and  $\Delta k$  parameters of the wavelet  $\psi_s$  by fitting it to  $h_G$ . Such a fit is shown in figure 2.8(b). The  $k_0$  and  $\Delta k$  values obtained from the wavelet's fit can be used as an alternative to the ones obtained from Lorentz fit to the spectrum. Both approaches give nearly identical results and can be used interchangeably.



Figure 2.8: (a) Comparison of the shape of the wavelet  $\psi_s(\theta)$  with the shape of  $h_L(\theta, r')$  and  $h_G(\theta, r')$ . We have set r' = 1.0 Å and s = 1.0. (b) Fit of the wavelet  $\psi_s$  to  $h_G$ . The fitted values are  $k_0 = 34.8$  Å<sup>-1</sup> and  $\Delta k = 11.9$  Å<sup>-1</sup>.

#### 2.4 A Simple absorber-scatterer system

We consider a simple point scatterer-absorber system from figure 2.2 and attempt to determine its structure. Structure determination in this case refers to the determination of  $\mathbf{r'}$  which is set, as before, to  $\mathbf{r'} = (0, 0, 3.19\text{\AA})$ . To do this we apply the wavelet transform, as defined in (2.42), to  $\bar{\chi}_{\text{Ga},\delta}$ . For a more compact notation we denote  $\bar{\chi}_{\text{Ga},\delta}$  as  $\bar{\chi}_{\delta}$  and write the wavelet transform  $\tilde{\chi}_{\delta}$  as

$$\widetilde{\chi}_{\delta}(\hat{\mathbf{k}}_{0},s) = \int_{\Omega} \psi_{\hat{\mathbf{k}}_{0},s}(\hat{\mathbf{k}}) \bar{\chi}_{\delta}(\hat{\mathbf{k}}) \mathrm{d}\Omega.$$
(2.47)

The wavelet transform  $\tilde{\chi}_{\delta}$  can be considered as an analogue of the point spread function which describes the response of the CSWT to a point input.

The integral in (2.47) was calculated numerically with the YAWTB toolbox (Jacques et al. 2001). The obtained wavelet transform is shown in figure 2.9. The calculation was performed for both  $h_L$ and  $h_G$ . For  $h_L$  the wavelet parameters were set to the ones obtained from the Lorentz fit to the effective spectrum. For  $h_G$  the wavelet parameters were set to the ones obtained from the fit of the wavelet to  $h_G$  as in figure 2.8(b).

A 3D view of the wavelet transform for  $h_G$  is presented in figure 2.9(a). The wavelet transform can be directly interpreted as a 3D image of the structure around the absorbing Ga atom. Here the word "structure" is an exaggeration since there is just one point scatterer around the Ga atom. Clearly the position of the scatterer can be determined. The wavelet transform has a maximum at (0, 0, 3.20 Å) which is almost exactly where the point scatterer was located. A slice of the transform in the x - z plane is presented in figure 2.9(b). The slice is divided into two halves. The left hand side corresponds to  $h_G$  whereas the right hand side corresponds to  $h_L$ . The maximum in the  $h_L$ half is located at 3.05 Å and is slightly shifted from the exact position of the scatterer. In general, however, one can draw the same conclusions from both halves of the image.

To give a more quantitative discussion of the 3D wavelet transform we derive analytic expressions for the profiles of  $\tilde{\chi}_{\delta}$  along r (this is equivalent to z) and  $\theta$  at r = r'. Here it becomes clear why we have kept the Lorentz approximation. The integrals that we will calculate are hard to evaluate for the Gumbel distribution due to the Gamma function in  $h_G$ . Yet, the results for the Lorentz approximation are quite general and can be extended to the numerical calculations with the Gumbel approximation.

### 2.4.1 RADIAL RESOLUTION

To obtain an analytic expression for  $\tilde{\chi}_{\delta}$  along the z axis which is in this case equivalent to the distance r from the absorber we set  $\theta$  to zero and assume that the scatterer is placed at  $\mathbf{r}' = (0, 0, r')$ . We



Figure 2.9: Wavelet transform  $\tilde{\chi}_{\delta}$  of a point-scatterer absorber system from 2.2. (a) A three dimensional view of the wavelet transform which was calculated for the Gumbel approximation, i.e.,  $h_G$ was used in  $\bar{\chi}_{\delta}$ . (b) A  $r - \theta$  slice of the wavelet transform from (a). The slice plane is in the z - xplane and passes through the origin, i.e., the position of the absorber. The left part of the plot was computed for the Lorentzian approximation while the right plot for the Gumbel approximation. (c) Profile along the white vertical line in (b). (d) Profile along the dashed circle in (b). In (c) and (d) the dots and the dashed red line represent numerical calculations for the Lorentzian and Gumbel approximations of the effective spectrum, respectively. The solid blue lines are given by  $\tilde{\chi}_{\delta}(z, r')$  and  $\tilde{\chi}_{\delta}(\theta)$ . The plots are normalized to their maxima for the comparison to be possible.

write the integral in (2.47) as

$$\widetilde{\chi}_{\delta}(r,r') = \int_{0}^{2\pi} \int_{0}^{\pi} \overline{\chi}_{\delta}(\theta,r')\psi(\theta,r)\sin\theta \mathrm{d}\theta \mathrm{d}\phi.$$
(2.48)

Due to technical reasons it is much easier to evaluate this integral without the small angle approximation, i.e., by replacing  $\theta^2$  in  $\bar{\chi}_{\delta}(\theta, r')$  and in  $\psi(\theta, r)$  with  $\sqrt{2-2\cos\theta}$ . We also assume that  $e^{-\Delta k(r+r')} \to 0$ , since  $\Delta k(r+r') \gg 1$ . For example for the I12 Diamond spectrum  $\Delta k(r+r') =$  $15.8 \times (1.0 + 3.19) = 66.2$ , where we have put r = 1.0 Å. Now the integral in (2.48) can be approximated as (Dul & Korecki 2012)

$$\widetilde{\chi}_{\delta}(r, r') \approx \frac{4\pi r_{\rm e}\beta(r/r_0)^{1/2}}{k\left[(r-r')^2 + \beta^2(r+r')^2\right]}.$$
(2.49)

Equation (2.49) is plotted in figure 2.9(c) were we see that it agrees perfectly with the numerical calculation. Its maximum is shifted from the exact position of the scatterer by

$$r_{\rm shift} = \frac{2r'(1+2\beta^2 - \sqrt{(1+\beta^2+\beta^4))}}{3(1+\beta^2)}.$$
(2.50)

For our example this shift is equal to 0.14 Å. The shift grows linearly with r' implying that most reliable results can be expected for local structure studies.

From equation (2.49) we can also evaluate an important quantity, namely the radial resolution. To do this we first note that the square bracket in the denominator in (2.49) can be written as  $[(r - r')^2 + (2\beta r')^2]$  since in the vicinity of r',  $r \approx r'$ . In this form the denominator is the same as for a Lorentz distribution and we can easily determine the full width at half maximum  $\Delta r$  which is equal to (Dul & Korecki 2012)

$$\Delta r \approx 4\beta r'. \tag{2.51}$$

 $\Delta r$  can be used to define the resolution of the CSWT. This result has already been predicted by Korecki, Novikov & Tolkiehn (2009). For our point-scatterer example  $\beta = 0.22$  and  $\Delta r = 2.79$ Å.

The resolution of the CSWT depends both on the parameters of the effective spectrum as well as on the distance from the absorber. Already at this point it can be argued that the CSWT will be able to distinguish only atoms which are relatively close to the absorbing atoms. With a constant value of  $\beta$ , further from the absorber, the linear term r' in (2.51) will make the resolution poor and the distinction of individual atom hardly possible.

## 2.4.2 Angular resolution

The next step in the quantitative description of the CSWT, as applied to white beam XFH, is to estimate the angular resolution. To do this we calculate the profile along the left half of the dashed

circle in figure 2.9(b). The CSWT can be written as

$$\widetilde{\chi}_{\delta}(\theta, r') = \int_{0}^{2\pi} \int_{0}^{\pi} \overline{\chi}_{\delta}(\theta', r') \psi(\theta' + \theta, r') \sin \theta' d\theta' d\phi$$
(2.52)

This integral is difficult to calculate, therefore we make the following simplification. The holographic signal as well as the wavelet are localized around z, i.e., the forward scattering direction. Far from the north pole their values are zero. It is then possible to approximate the surface of the sphere, close to the north pole, by a plane and instead of integrating over a full sphere integrate over the whole plane. The integration variable  $\theta'$  will then be equal to  $\theta' = \sqrt{\theta_x^2 + \theta_y^2}$  and the differential area element to  $\sin \theta' d\theta' d\phi \mapsto d\theta_x d\theta_y$  with the integration limits going from minus infinity to infinity. Both  $\bar{\chi}_{\delta}$  and the wavelet are circularly symmetric around the z axis which allows us to choose the x direction as the direction in which the correlation is calculated. With the transition from a sphere to a plane  $\tilde{\chi}_{\delta}(\theta, r')$  is equal to

$$\widetilde{\chi}_{\delta}(\theta, r') \approx \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \bar{\chi}_{\delta} \left( \sqrt{\theta_x^2 + \theta_y^2}, r' \right) \psi \left( \sqrt{(\theta_x + \theta)^2 + \theta_y^2}, r' \right) \mathrm{d}\theta_x \mathrm{d}\theta_y.$$
(2.53)

This integral can be evaluated to (Dul & Korecki 2012)

$$\widetilde{\chi}_{\delta}(\theta, r') \approx \frac{\pi r_{\rm e} r' r_0 {\rm e}^{-(\beta^2 + 1)q' \theta^2/(2\beta)}}{2q' \beta (r' r_0)^{3/2}} \left[ 1 - \beta \, {\rm e}^{q' \theta^2/(2\beta)} \sin\left(\frac{q' \theta^2}{2}\right) \right],\tag{2.54}$$

where  $q' = k_0 r'/2$ . Equation (2.54) is compared with the exact numerical result in figure 2.9(d) and the agreement is very good. We now define the angular resolution  $\Delta\theta$  as the position of the first zero of  $\tilde{\chi}_{\delta}(\Delta\theta, r')$ . It can be estimated by writing  $\sin(q'\theta^2/2) \approx q'\theta^2/2$  and solving  $\tilde{\chi}_{\delta}(\Delta\theta, r') = 0$ . The result is (Dul & Korecki 2012)

$$\Delta \theta = \sqrt{2\frac{\beta}{q'}} \sqrt{W\left(\beta^{-2}\right)},\tag{2.55}$$

where W is the Lambert W function (Corless et al. 1996). For the I12 Diamond spectrum  $\Delta \theta = 7.46^{\circ}$  which is equivalent to 0.42 Å in the tangential plane at 3.19 Å. An important difference between the angular resolution and the radial resolution is their dependence on r'. In contrast to  $\Delta r$ ,  $\Delta \theta$  decreases with the distance from the absorber. In other words, atoms which will be further from the absorber will be better localized and separated.

### 2.5 Chain of point scatterers

In the previous section we have applied the CSWT to a simple point-scatterer absorber system and we have shown that its structure can be reconstructed. In this section we complicate the matter and consider a chain of point scatterers. This is a "toy" model for realistic chains of atoms. First



Figure 2.10: The point scatterer chain model and the wavelet transform of the hologram of the chain. (a) Schematic view of the considered point scatterer chain. (b) Profile of the wavelet transform along the chain. The open circles denote numerical results obtained with the Lorentz approximation of the effective spectrum, whereas the filled circles denote numerical results obtained with the Gumbel approximation. The dashed doted lines represent contributions from the first three scatterers to the Gumbel result. The solid red line is the analytic result given by equation (2.57). The dashed vertical lines mark the positions of the first six scatterers in the chain.

attempts to analyze atomic chains with the CSWT were made by Korecki et al. (2011), however, their discussion lacked any quantitative results.

The model of our scatterer chain is presented in figure 2.10(a). We assumed that the chain starts at the origin with an absorbing atom and consists of M equally spaced scatterers. The scatterers are separated by  $\Delta d$  and we align the chain along the z axis. A white beam hologram for such a chain can be written as

$$\bar{\chi}_{\text{chain}} = \sum_{m=1}^{M} \bar{\chi}_{\delta}(\theta, r = m\Delta d), \qquad (2.56)$$

i.e., as a sum of holograms from each scatterer in the chain. We set  $\Delta d = 3.19$  Å and M = 100and denote the CSWT of  $\bar{\chi}_{\text{chain}}$  as  $\tilde{\chi}_{\text{chain}}$ . The profile of  $\tilde{\chi}_{\text{chain}}$  is shown in figure 2.10(b). The calculation was performed for both Lorentz and Gumbel approximations of the effective spectrum. The CSWT has one distinct strong maximum, a very weak second maximum and a long tail. The strong maximum is at the position of the first scatterer whose CSWT mainly contributes to the maximum. The weak maximum is at the position of the second scatterer. Signals from other scatterers contribute mainly to the continuous tail. The profile in figure 2.10(b) can be estimated for an infinite chain  $(M \to \infty)$  and for the Lorentzian approximation to the effective spectrum. The analytic expression for  $\tilde{\chi}_{chain}$  is given by (Dul & Korecki 2012)

$$\widetilde{\chi}_{\text{chain}} = \sum_{m=1}^{\infty} \widetilde{\chi}_{\delta}(r, m\Delta d) 
= -\frac{\pi r_{\text{e}} \sqrt{r/r_0}}{k_0 r \Delta d} \text{Im} \left[\psi_0(\xi) - \psi_0(\xi^*)\right],$$
(2.57)

where  $\xi$  ( $\xi^*$  denotes the complex conjugate) is given by

$$\xi = 1 + \frac{r(\beta^2 - 2i\beta - 1)}{\Delta d(\beta^2 + 1)}$$
(2.58)

and  $\psi_0$  is the polygamma function (Olver et al. 2010). The profile given by (2.57) is plotted in figure 2.10(b) with a solid red line. In the nearest neighborhood of the absorber it agrees with the numerical calculation very well. It confirms that the CSWT is sensitive to the local structure of the absorbing atom. In real conditions we can expect to determine the position of at least the first scatterer (atom).

### 2.6 Application to GaN

In the previous two sections we have applied the CSWT to model systems such as the point scattererabsorber system and a chain of point scattering objects. With these systems we have gained insight to what structure information can be obtained from the CSWT as applied to white beam XFH. In this section we develop the method further by applying it to a more realistic system, namely gallium nitride (GaN). Gallium nitride is a III/V bandgap semiconductor with a variety of applications in electronics especially in high-power/frequency transistors and light emitting diodes. It can be also doped with transition metals and/or rear earth impurities in which case it exhibits ferromagnetic properties. In this sense doped GaN belongs to a class of materials known as diluted magnetic semiconductors which have a variety of interesting properties and potential application in spin transport electronics (Dietl 2010, Dietl & Ohno 2014). In this section we focus on imaging of local atomic structure in gallium nitride (GaN). First around gallium atoms and later around impurities.

The structure of GaN is presented in figure 2.11(a). It is a wurtzite crystal structure with the corresponding  $P6_3mc$  space group and lattice constants equal to a = 3.186 Å and c = 5.178 Å. In GaN only gallium atoms emit fluorescence photons for hard x-ray spectra. We concentrate on local

structure imaging around these atoms. There are two nonequivalent positions of gallium atoms in the GaN lattice. They are marked as Ga<sub>1</sub> and Ga<sub>2</sub> in figure 2.11(a). By nonequivalent positions we mean that the surrounding of Ga<sub>1</sub> is different from the surrounding of Ga<sub>2</sub>. This can be easily observed if one compares the location of the nearest neighbors of both Ga<sub>1</sub> and Ga<sub>2</sub>. Since there are two nonequivalent gallium positions the hologram from gallium atoms will be an average of the holograms from Ga<sub>1</sub> and Ga<sub>2</sub>, namely  $\chi_{\text{Ga}} = (\chi_{\text{Ga}_1} + \chi_{\text{Ga}_1})/2$ .

We have simulated the  $\chi_{\text{Ga}_1}$  and  $\chi_{\text{Ga}_2}$  holograms for 100 Å atomic clusters. Formula (2.11) was used for the calculation. The calculation was performed on a  $401 \times 801$  ( $\theta \times \phi$ ) grid. The  $\theta$  range was limited to  $25^{\circ} - 88^{\circ}$  to mimic typical experimental conditions. The region around the pole ( $\theta = 0^{\circ}$ ) is usually occupied by the detector and for grazing angles, i.e., close to the equator ( $\theta = 90^{\circ}$ ), our theory is not fully applicable. Finally, a Poisson-like noise which corresponded to  $10^{7}$  photons per pixel was added to the final hologram.



Figure 2.11: (a) GaN unit cell. (b) Possible impurity positions in the GaN lattice O'Donnell & Dierolf (2010).

The simulated  $\chi_{\text{Ga}}$  hologram is presented in figure 2.12(a). The two most vivid features of the hologram are the dark spots and bands. If we compare the hologram with the projection of the crystal structure around gallium atoms in GaN [figure 2.12(b)] the real space nature of the hologram becomes evident. This has already been noted in the past by Korecki & Materlik (2001) and described in detail by Korecki, Tolkiehn & Novikov (2009). The dark spots can be attributed to signals from atomic rows. The bands are similar in nature to Kossel or Kikuchi lines that we met in Section 1.1. Figure 2.12(c) presents the projections of some of the lattice planes in a hexagonal GaN lattice. If we compare figures 2.12(a) and 2.12(c) we can see a one to one correspondence between the bands

 $(10\bar{1}0)$ (a) (b) (c)  $(11\bar{2}0)$  $(1\bar{2}10)$  $(01\bar{1}0)$ x 10 10 [100] [010] Ga - double  $(\bar{1}101)$ 1001  $(10\overline{1}1)$ Ga occupancy

in the white beam hologram and the plane projections. One can also say that the hologram gives us direct information about the long range order around the absorbing atoms.

Figure 2.12: (a) A white beam x-ray fluorescence hologram simulated for gallium atoms in wurtzite GaN. The inner dashed circle marks  $\theta = 25^{\circ}$ , the outer dashed circle marks  $\theta = 88^{\circ}$  and the outer solid circle marks  $\theta = 90^{\circ}$ . For a better presentation of data the right hand side of the hologram has no noise. (b) Projection of the crystal structure in GaN as seen from the gallium atoms Ga<sub>1</sub> and Ga<sub>2</sub>. The atoms are represented by balls and their size is proportional to their atomic number and inversely proportional to their distance from the central gallium atoms. (c) Projection of low-index lattice planes, in the hexagonal GaN lattice, onto a sphere. (a) and (b) are taken from Dul & Korecki (2012)

If we apply the CSWT to  $\chi_{\text{Ga}}$  the wavelet transform space should resemble the structure around gallium atoms in GaN. A slice of the CSWT, which was calculated for scales which corresponded to distances from 1 Å to 20 Å away from the absorber, is presented in figure 2.13. The radial scale in the image was set to  $\sqrt{r}$  for better presentation. In the left half of the image the signal from nearest nitrogen atoms was removed. In the right half of the image the signal from the nearest nitrogen atoms is present. This was done to check the sensitivity of white beam XFH and its wavelet analysis to the imaging of light atoms. The expected positions of atoms are marked with white circles up to 10 Å. The size of the circles is inversely proportional to their distance from the absorber.

A close inspection of figure 2.13 reveals that in this case the wavelet transform space very poorly resembles the structure around the absorbing gallium atoms. Most importantly the atoms are displaced from their nominal positions. The shift is especially visible in the case of the nearest neighbor nitrogen atoms which are marked with arrows. To see the shift one needs to compare the left side of the image (nearest nitrogens absent) with the right side (nearest nitrogens present). On the right half the nitrogen signal is outside the white circle that marks its expected position (the larges circle which is closet to the white dot). The most intense maxima which correspond to nearest neighbor



Figure 2.13: The continuous spherical wavelet transform of the  $\chi_{\text{Ga}}$  hologram from figure 2.12(a) (Dul & Korecki 2012). The figure shows a 2D  $r - \theta$  slice in the  $(1\overline{2}0)$  plane. The expected positions of atoms have been marked up to 10 Å with white circles. The left half of the plot corresponds to a situation in which the signal from the nearest neighbor nitrogen atoms has been removed from  $\chi_{\text{Ga}}$ . The expected positions of nearest nitrogen and gallium atoms are marked with arrows and labels. The position of the absorbing atom is marked with the central white dot.

gallium atoms are also shifted, yet by a smaller margin then the nitrogen ones. Apart from the shifts there is a number of artifacts which appear in the image. Some of these are marked with squares. Note that the artifact marked with the central square appeared in an angular region in which there was no holographic signal. Above it there are additional maxima which cannot be attributed to atoms. In real applications such artifacts can make the analysis cumbersome and/or lead to false conclusions.

The distorted like character of figure 2.13 is due to the non orthogonality of the holographic signal  $\chi_i$  and the chosen wavelet family  $\psi$ . This non orthogonality manifests itself as a non Dirac delta like shape of  $\tilde{\chi}_{\delta}(r, r')$  and  $\tilde{\chi}_{\delta}(r', \theta)$ . Most of the features in figure 2.13 originate from the cone-like structure in figure 2.9(a). In the case of more than one scattering objects the cone-like structures from distinct scatterers overlap and produce artifacts and shifts. Since, the shape of a white hologram is given by equation (2.9) or more precisely by the Fourier transform of the effective spectrum N(k), presumably, it should be possible to adjust the shape of the effective spectrum in such a way as to minimize the number of artifacts and distortions. In fact, for a monochromatic beam this is achieved by setting  $N(k) = \delta(k - k_0)$ , however, in this case twin images appear which are difficult to remove. One could also try to minimize the artifacts by keeping the shape of the effective spectrum as it is and adjusting its parameters  $k_0$  and  $\Delta k$ . This should be done in such a way as to minimize  $\Delta r$  and  $\Delta \theta$  for the best resolution.

## 2.6.1 The inverse windowed wavelet transform

Clearly, the reconstruction obtained in figure 2.13 is of poor quality and does not permit reliable structure analysis. At this point one might conclude that the whole effort was in vain. Fortunately, there is still a way to obtain valuable structure information from our wavelet transform. The whole process is based on the calculation of the inverse wavelet transform in a limited range of scales (Korecki, Novikov & Tolkiehn 2009). This can be achieved by introducing a window function w(s)in the inversion formula (2.44). The window function is defined as

$$w(s) = \begin{cases} 1, & s_{\rm c} \le s \le s_{\rm b} \\ 0, & \text{elsewhere,} \end{cases}$$
(2.59)

where  $s_c = (r_c/r_0)^{-1/2}$ ,  $s_b = (r_b/r_0)^{-1/2}$  and the inversion formula (2.44) reads

$$F_i(\hat{\mathbf{k}}) = \frac{1}{C_\delta} \int_0^\infty \tilde{\chi}_i(\hat{\mathbf{k}}, s) w(s) \frac{\mathrm{d}s}{s^2}.$$
(2.60)

The  $C_{\delta}$  constant is given by equation (2.45) and for the wavelet in (2.46) is equal to

$$C_{\delta} = \left[\pi \arccos(\beta^{-1})\right] / (k_0 r_0).$$

The  $s_c$  and  $s_b$  parameters define the range of scales for which the transform is effectively calculated. In terms of the distances from the absorbing atoms the inverse is calculated in the range from  $r_b$  to a cutoff distance of  $r_c$ ,  $r_b$  and  $r_c$  are required to fulfill  $r_0 \leq r_b < r_c$ . If w(s) = 1 then the inverse yields the original hologram  $F_i(\hat{\mathbf{k}}) \simeq \bar{\chi}_i(\hat{\mathbf{k}})$ . Equation (2.60) can be treated as a filter which excludes signals from atoms that lie outside the  $\langle r_b, r_c \rangle$  range.

Equation (2.60) can be termed as the inverse windowed wavelet transform (IWWT). It has been applied to white beam holographic data to obtain 2D projections of the local structure around absorbing atoms (Korecki, Novikov & Tolkiehn 2009, Korecki et al. 2011). However, the direct usage of equation (2.60) is computationally involving and not practical. It requires an in between calculation of  $\tilde{\chi}_i$  with equation (2.42) which serves as an input to equation (2.60). Therefore, we rewrite equation (2.60) as

$$F_{i}(\hat{\mathbf{k}}) = \frac{1}{C_{\delta}} \int_{S^{2}} \bar{\chi}_{i}(\hat{\mathbf{k}}') \left[ \int_{0}^{\infty} \psi_{\hat{\mathbf{k}},s}(\hat{\mathbf{k}}')w(s)\frac{\mathrm{d}s}{s^{2}} \right] \mathrm{d}\Omega'$$
$$= \frac{1}{C_{\delta}} \int_{S^{2}} \bar{\chi}_{i}(\hat{\mathbf{k}}') \left[ \mathcal{R}_{\hat{\mathbf{k}}}\Psi(\hat{\mathbf{k}}') \right] \mathrm{d}\Omega'.$$
(2.61)

The action of the rotation operator  $\mathcal{R}_{\hat{\mathbf{k}}}$  is defined in (2.41). For the scaled mother wavelet from equation (2.46) the quantity  $\Psi(\hat{\mathbf{k}}) = \Psi(\theta)$  can be evaluated to (Dul & Korecki 2012)

$$\Psi(\theta) = \frac{1}{2q_0\theta^2} \left[ e^{-\beta q_0\theta^2/s_c^2} \sin\left(\frac{q_0\theta^2}{s_c^2}\right) - e^{-\beta q_0\theta^2/s_b^2} \sin\left(\frac{q_0\theta^2}{s_b^2}\right) \right].$$
 (2.62)



Figure 2.14: Projections of the local atomic structure obtained from  $\chi_{\text{Ga}}$  through the inverse windowed wavelet transform [compare with figure 2.11(b)]. (a) Projection around Ga atoms obtained for  $r_c = 5\text{\AA}$ . (b) Angular profile along the white line in (a) from  $\theta = 0^\circ$  to  $\theta = 90^\circ$ . The solid line represents the signal from all the atoms, the dashed line the signal with nearest neighbor nitrogen atoms subtracted and the dotted line the signal with both nearest neighbor nitrogen and gallium atoms subtracted. The angular positions of atoms up to 5 Å are marked with vertical lines with triangles. The height of the lines is proportional to the expected signal. Figure (c) and (d) are analogous to (a) and (b) but have been calculated for  $r_c = 10$  Å. In (d) the vertical lines mark atoms up to 10 Å. This image is taken from (Dul & Korecki 2012)

Equation (2.61), together with (2.62), allows one to evaluate the inverse windowed wavelet transform directly from the hologram in a fast single step.

The inverse windowed wavelet transform of the gallium hologram  $\chi_{Ga}$  is shown in figure 2.14. It was calculated for two values of  $r_c$ , i.e.,  $r_c = 5 \text{ Å}$  [figures 2.14(a) and 2.14(b)] and  $r_c = 10 \text{ Å}$  [figures 2.14(c) and 2.14(d)]. The  $r_b$  parameter was set to  $r_b = r_0 = 1$  Å. In the left halves of the images the nearest nitrogen atoms have been removed. If one compares figures 2.14(a) and 2.14(c) with the GaN crystal structure projection around gallium atoms from figure 2.12(b) then one can establish a direct correspondence between the IWWT image and the projection. Owing to the localization of the white beam holographic signal the IWWT image can be interpreted as a projection of the local atomic structure around the absorbing atom. All the visible maxima in figure 2.14(a) can be attributed to signals from atoms. Signals from atoms which are further away from the absorbing atom than 5 Å are strongly suppressed. In figure 2.14(c) atoms that are further away from the absorbing atom than 10 Å are strongly suppressed. Signals from atoms that lie between 5 - 10 Å are clearly visible. If we compare the left and right sides of the images we see that the signal from nearest nitrogen atoms is also clearly visible. Finally, the IWWT images are nearly free form artifacts. The degree of their suppression can be seen in the region around the pole ( $\theta = 0^{\circ}$ ). In figure 2.13 the maximum marked with the central square had an amplitude that was comparable with the most intense, true maxima. In the IWWT images there is only a faint maximum inside the inner dashed circle and its amplitude is much lower then the amplitude of the most intense true maxima.

A more detailed analysis of the IWWT images is possible if one examines the profiles along the  $(1\bar{2}0)$  plane, i.e., figures 2.14(b) and 2.14(d), or equivalently along the white line from  $\theta = 0^{\circ}$  to  $\theta = 90^{\circ}$ . The angular positions of atoms are given by vertical lines with triangles. The height of these lines is proportional to the expected signal. There are three curves visible in the profiles. The solid curve was calculated when all atoms were present in the atomic cluster. The dashed line was calculated with the nearest neighbor nitrogen atoms removed. In the case of the dotted line both nearest nitrogens and gallium atoms were removed. These curves depict how the IWWT signal is formed. The signals from distinct atoms add up. When an atom is isolated in the  $\theta$  direction there is a clear maximum which gives its angular position [as for the nearest gallium atoms in figure 2.14(b)]. When atoms are in close proximity of one another then their signals overlap forming complex structures. This is especially visible for nearest nitrogen atoms in figure 2.14(b) and nearest gallium atoms in figure 2.14(d). The overlapping of the signal means that the analysis needs to be preformed for more than one value of  $r_c$  to distinguish between the different atoms.  $r_c$  must also not be to large since that increases the overlap.

As a final and general remark on the IWWT let us discuss some of its limitations. The wavelet transform space which is shown in figure 2.9(a) and 2.13 can be interpreted as a 3D image of the atomic arrangements around the absorbing atoms, yet the image, especially for complex systems like GaN, is distorted by artifacts. On the contrary, the IWWT is nearly free from artifacts. However,

the IWWT offers only 2D projections of atomic structure around absorbing atoms and has a very limited radial resolution. The limited radial resolution is due to the integral over scales in equation 2.60. Especially, if two atoms, one after the other, are present in a atomic chain then only the first can be identified by an appropriate choice of  $r_c$ . On the one hand, this is a setback from our goal of direct three dimensional imaging of local atomic structure around absorbing atoms. On the other hand, the method provides unique angular resolution and could be combined with other techniques, e.g., XAFS to obtain a full 3D picture.

#### 2.6.2 LOCATION OF IMPURITY SITES

The main advantage of XFH is the ability to selectively choose elements in the crystal lattice and obtain local structure information around them. For white beam XFH we have shown that it is possible to obtain 2D projections of the local structure around the absorbing atom. It is also possible to obtain a limited glimpse into the third dimension by adjusting the window width of the IWWT. Herein, we would like to show that white holograms together with their IWWT transforms can be used for other purposes, namely the location of impurities in the crystal lattice. We will concentrate on impurities that occupy many crystallographically nonequivalent sites. Our main goal is to propose an automatic procedure which can be used to locate such impurities.

To visualize the problem, let us start from an example and consider a few possible impurity sites in GaN. There are a variety of positions that impurities can occupy in the GaN lattice (O'Donnell & Dierolf 2010). To keep the discussion simple we limit our considerations to four possible sites: the Ga and N substitutional sites and the octahedral (O) and tetrahedral (T) interstitial sites. These sites are schematically shown in figure 2.11(b). For each of these sites there are two nonequivalent sites in the crystal lattice, e.g.,  $T_1$  and  $T_2$  for the tetrahedral site. At this point it is important to specify the type of the impurity atom. This introduces an overwhelming number of possibilities which can be reduced if we assume that equation (2.14) holds. In this way the impurity holograms will depend only on the site that the impurities occupy and will be approximately independent of their type. As a result, the hologram for the substitutional Ga site will be identical to the one in figure 2.12(a). The holograms for each of these sites were calculated as an average over the two nonequivalent sites, e.g., the T site hologram was calculated as  $\chi_T = (\chi_{T_1} + \chi_{T_2})/2$ . Figure 2.15 also depicts projections of the crystal structure around each of the impurities and the IWWT images of the holograms. The IWWT images have been calculated for  $r_b = r_0 = 1$  Å and  $r_c = 10$  Å.

A few interesting conclusions can be drawn from figure 2.15. We start from the holograms. If one compares the holograms for the N ( $\chi_N$ ) and T ( $\chi_T$ ) sites than one can conclude that they are similar. By this we mean the shade of the bands in both holograms. To the contrary, the hologram for the O ( $\chi_O$ ) site is completely different from  $\chi_N$  and  $\chi_T$ . The hologram for the Ga site in figure



Figure 2.15: Simulated white beam holograms and IWWT images for impurities in GaN located at the substitutional N, the octahedral (O) and tetrahedral (T) sites (Dul & Korecki 2012). The left halves of the holograms have noise added to them and the right halves are noise free for better presentation.

2.12(a) also differs from the ones presented in figure 2.15.

Now we turn our attention to the IWWT images. If we compare the IWWT images for the N and T sites then we can conclude that these are completely different from one another. On the other hand, the IWWT images for the T and O sites posses some similarities, most notably, in the placement of the strongest maxima and the maxima closest to the inner dashed circle. It needs to be noted that all the IWWT images in figure 2.15 differ significantly from the IWWT image for the Ga substitutional site from figure 2.14(c).

Hence, from the above analysis it can be concluded that the position of the impurity in the crystal lattice can be determined from its hologram and the corresponding IWWT image. In principle, one could attempt to extract such information from just one of these, either the hologram or the IWWT image. However, due to the similarities between the holograms (e.g., the holograms for the N and T sites) and the IWWT images (e.g., the IWWT images for the T and O sites) such an approach might lead to ambiguities. We will actually stumble upon such ambiguities in due course.

Let us assume that one has obtained a hologram for an impurity from an experiment. One is interested where the impurity is located in the crystal lattice. By examining the hologram and its IWWT one can determine the position of the impurity. For this, one has to compare the hologram and the IWWT image with other holograms and IWWT images generated for possible sites that the impurity can occupy. Of course, this can be done by hand. However, it is also possible to introduce an automatic procedure.

Let us denote the hologram for the impurity with  $\chi_{\text{Imp}}$  and its IWWT as  $F_{\text{Imp}}$ . These will be our inputs. We take the following steps to determine the sites that the impurity occupies:

- 1. The unit cell of the considered crystal is divided into a grid of X points.
- 2. For each point x in the grid a hologram  $\chi_x$  is generated as if the impurity was placed at this point. The hologram is generated for a small cluster of atoms, a few Ångström in diameter.
- 3. The IWWT  $F_x$  of  $\chi_x$  is calculated with an appropriately chosen window.
- 4. For each point x the following R-factor is calculated:

$$R_{x} = \frac{\sum_{c} \left[ (F_{\rm Imp})_{c} - (F_{x})_{c} \right]^{2}}{\sum_{c} \left[ (F_{\rm Imp})_{c} + (F_{x})_{c} \right]^{2}},$$
(2.63)

where the c sum runs over the pixels in  $F_{\text{Imp}}$  and  $F_x$ . As a result to each point x in the unit cell a number  $R_x$  can be attributed. The lower the value of  $R_x$ , the more probably it is that the impurity occupies a positions in the unit cell given by x. Since the IWWT images, for different sites, might be similar (see figure 2.15) there might be a number of fake minima in the  $R_x$  space. To eliminate the fake minima in  $R_x$  we denoted with S the set of all the most distinct minima in  $R_x$ . The S set will have  $n_s$  elements.

- 5. For each minimum s in S a hologram  $\chi_s$  is generated. The hologram has to be generated for a relatively large cluster of atoms so that distinct bands are visible.
- 6. It is assumed that the  $\chi_{\rm Imp}$  hologram can be expressed as

$$\chi_{\rm Imp} = \sum_{s \in S} f_s \chi_s, \tag{2.64}$$

where the s sum runs over the minima in  $R_x$ . The  $f_s$  coefficients describe the contribution of each of the  $\chi_s$  holograms to  $\chi_{\text{Imp}}$ .

7. The following system of linear equations is solved to find the  $f_s$  coefficients

$$(\mathbf{A}^{\mathrm{T}}\mathbf{A})\mathbf{f} = \mathbf{A}^{\mathrm{T}}\mathbf{b},\tag{2.65}$$

where the **f** vector contains the  $f_s$  coefficients  $\mathbf{f} = (f_1, f_2, ..., f_{n_s})^{\mathrm{T}}$  and the **b** vector is formed from the experimental hologram, namely  $\mathbf{b} = [(\chi_{\mathrm{Imp}})_{11}, ..., (\chi_{\mathrm{Imp}})_{N(M-1)}, (\chi_{\mathrm{Imp}})_{NM}]^{\mathrm{T}}$ . The **A** matrix is defined as

$$\mathbf{A} = \begin{pmatrix} (\chi_{s_1})_{11} & (\chi_{s_1})_{12} & (\chi_{s_1})_{13} & \cdots & (\chi_{s_1})_{N(M-1)} & (\chi_{s_1})_{NM} \\ (\chi_{s_2})_{11} & (\chi_{s_2})_{12} & (\chi_{s_2})_{13} & \cdots & (\chi_{s_2})_{N(M-1)} & (\chi_{s_2})_{NM} \\ \vdots & & \ddots & & \vdots \\ (\chi_{s_n})_{11} & (\chi_{s_n})_{12} & (\chi_{s_n})_{13} & \cdots & (\chi_{s_n})_{N(M-1)} & (\chi_{s_n})_{NM} \end{pmatrix},$$
(2.66)

where  $\chi_{s_1}$  is the first and  $\chi_{s_n}$  the last hologram in the sum in equation (2.64). It is assumed that  $\chi_{\text{Imp}}$  and  $\chi_s$  are represented by  $N \times M$  matrices.

8. The fake minima in  $R_x$  should be attributed with  $f_s$  coefficients that are zero.

Let us given an example of the proposed procedure for the T site in GaN. We take the T hologram and its IWWT image as the input ( $\chi_{Imp} = \chi_T$  and  $F_{Imp} = F_T$ ). For simplicity we consider only the (1 $\overline{20}$ ) plane (5.53 Å × 5.17 Å) as in figure 2.11(b) and slice it into a 35 × 32 grid of points. For each point x we calculate a small hologram and its IWWT. The small holograms are calculated for 10 Å clusters. Then for each point x we calculate the R-factor  $R_x$ . The obtained R-factor map is presented in figure 2.16(a). A few distinct minima can be seen in this map. The two most intense ones coincide with the  $T_1$  and  $T_2$  sites. They have a FWHM of 0.96 Å in the vertical direction and 0.83 Å in the horizontal one. The weaker minima coincide with the N and O sites. Thus, there are six potential positions ( $n_s = 6$ ) in the (1 $\overline{20}$ ) plane that the impurity can occupy. For each of these minima we generate a hologram as if the impurity was placed at the position of the minimum. These six holograms are generated for large 60 Å clusters of atoms. We solve equation (2.65) and obtain six f<sub>s</sub> coefficients. They are plotted in 2.16(b). The weak minima have f<sub>s</sub> values that are nearly



Figure 2.16: Reconstruction of the impurity position (T site) in the GaN lattice (Dul & Korecki 2012). (a) The R-factor map in the  $(1\overline{2}0)$  plane calculated with equation (2.63). (b) The  $f_s$  values obtained for the most intense minima. The circles coincide with the positions of the minima in (a).

zero and they can be ruled out. The strong minima which coincide with the  $T_1$  and  $T_2$  sites have  $f_s$  values which are nearly equal to 0.5, the values which were used to simulate  $\chi_T$ . Thus, we can conclude that the impurity occupies the  $T_1$  and  $T_2$  sites.

As a somewhat more complicated example, consider a impurity which is displaced from the Ga substitutional site by d in the  $[00\overline{1}]$  direction [c.f. figure 2.11(b)]. Such displaced sites have been reported, e.g., for Eu in GaN (O'Donnell & Dierolf 2010). There are two nonequivalent displaced Ga substitutional sites  $S_1$  and  $S_2$  in the GaN lattice. For an impurity that equally occupies these two sites the net hologram is calculated as  $\chi_S = (\chi_{S_1} + \chi_{S_2})/2$ . It is assumed that the impurity is shifted by d = 0.4 Å which is a rather large value which we chose for illustration purposes. In practice, for the introduced noise level, shifts as small as 0.1 Å could be detected. We apply the R-factor analysis to  $\chi_{Ga}$  and  $\chi_S$ . The corresponding R-factor maps are shown in figures 2.17(a) and 2.17(b). In figure 2.17(a) there are to clear distinct minima at the Ga<sub>1</sub> and Ga<sub>2</sub> positions. In figure 2.17(b) there are also two minima which are shifted from the original Ga<sub>1</sub> and Ga<sub>2</sub> positions. The positions of the minima coincide with the assumed positions of the impurity. In figure 2.17(c) the obtained  $f_s$  coefficients are given for the most intense minima in figure 2.17(b). Clearly, the only two minima whose  $f_s$  values are significantly different from zero are the ones that correspond to  $S_1$  and  $S_2$ .



Figure 2.17: Sensitivity of the R-factor/linear regression approach to small impurity shifts (Dul & Korecki 2012). (a) R-factor map for an impurity placed at substitutional Ga<sub>1</sub> and Ga<sub>2</sub> sites. (b) R-factor map for an impurity at the displaced S<sub>1</sub> and S<sub>2</sub> sites. (c)  $f_s$  coefficients for the S sites.

## 2.7 Conclusions

In this Chapter we have considered white beam XFH. Our most important contributions to the field are summarized in the points below. We have:

- introduced the Gumbel approximation of the effective spectrum which significantly improves the description of white beam holograms;
- provided a quantitative description of the continuous spherical wavelet transform when applied to white beam XFH by deriving formulas for the radial and angular resolution;
- explicitly shown, by considering a simple model of a chain of point scatterers, that the analysis of white beam holograms with the continuous spherical wavelet transform is sensitive to local atomic structure;
- derived a compact analytic expression [equation (2.62)] for the inverse windowed wavelet transform that allows its fast calculation in a single step;
- shown that the inverse windowed wavelet transform can be used to image light atoms. Our example concerned nitrogens in GaN; and
- developed a wavelet supported reliability factor (R-factor) analysis of white beam holograms with which the positions of impurities that occupy multiple lattice sites can be determined. The approach is sensitive to small shifts of the impurities from the regular lattice sites.

### 2. WHITE BEAM XFH AND WAVELETS

The most appealing feature of the continuous spherical wavelet transform as applied to white beam XFH is that it is a model free approach. This means that no *a priori* knowledge about the structure is required for it to work. Another feature of wavelets that needs to be mentioned is its insensitivity to missing data. In real experimental conditions it is hardly possible or at least difficult to measure the holograms in a full solid angle. In practice only a fraction of the full solid angle is measured and the problem of missing data arises. For monochromatic XFH the holographic signal from a single atom covers the whole surface of the sphere. When only part of the hologram is available, the reconstruction of atomic structure might be affected by truncation errors. For white beam holograms the signal from a single atom is localized around the forward scattering direction and the full information about the atom's position relative to the absorber is localized in a small area (patch) of the sphere. The wavelet analysis uses only the information contained in this patch avoiding truncation errors.

The obtained results focused mainly on future applications of white beam XFH. Most notably, the possibilities of location of impurities that occupy multiple lattice sites have been explored. Although, such possibilities have been briefly mention in the past (Korecki, Tolkiehn & Novikov 2009), they have been limited to simple, visual comparisons of holograms generated for different lattice sites. Herein, we have provided a robust approach that allows one to determine the locations of impurities with high precision. Our method could be useful for determining impurities that occupy minority sites (Pereira et al. 2012, 2014).

#### CHAPTER 3

# MATRIX EFFECTS IN MONOCHROMATIC XFH

X-ray fluorescence holography in the inverse mode is in its essence an absorption technique. It derives structure information from absorption effects inside the sample. The hologram can be considered as a direction and energy dependent oscillatory part of the photoionization cross section of the absorbing atoms. In an inverse mode XFH experiment the hologram is probed indirectly by measuring the number of fluorescence photons emitted from the sample. In Section 1.3 we have discussed how the holographic signal can be obtained from the measured x-ray fluorescence. In doing so, we have considered thin samples for which the number of fluorescence photons is directly proportional to the photoionization cross section. Direct proportionality between these two quantities is commonly assumed in XFH, however, by no means this is a general assumption. According to x-ray fluorescence spectroscopy (van Grieken & Markowicz 2001), it breaks down pretty quickly when the sample's thickness starts to increase. For thick samples, matrix effects, i.e., beam attenuation and indirect excitation, make the relation between the photoionization cross section and the measured fluorescence more complicated. In this chapter we examine how beam attenuation and indirect excitation can impact XFH and how one can correct for them. Our discussion is based on the work by Dul et al. (2013).

### 3.1 Origin of the problem

Consider a standard XFH experimental setup as in figure 3.1(a). A flat sample is illuminated by a monochromatic beam of x-rays. The sample has a thickness T and otherwise extends to infinity. The direction of the beam with respect to the sample is given by two angles  $\theta$  and  $\phi$ . We are interested in a hologram  $\chi_i$  from element i which is placed in a thin layer at a depth of t underneath the surface's sample. The thickness of the thin layer is equal to dt. Formally,  $\chi_i$  can be defined as an oscillation of the photoionization cross section  $\sigma_i$  and is given by equation (1.18) which we here recall

$$\sigma_i(\mathbf{k}) = \sigma_i^0(k) \left[ 1 + \chi_i(\mathbf{k}) \right]. \tag{3.1}$$

In XFH one attempts to access  $\chi_i$  by measuring the number of fluorescence photons  $Y_{i,\lambda}$  emitted by element *i* through a chosen emission line  $\lambda$ . If we assume that the sample is thin then we can write  $Y_{i,\lambda} \propto \sigma_i$  and obtain the same results as in Section 1.3. If the sample cannot be considered as thin then the situation becomes more complicated. To see what actually happens let us try to calculate the number of photons emitted by atoms of type *i* when the sample is thick. To do so we need to

consider two excitation processes of element *i*, i.e., direct excitation (DE) and indirect excitation (IE). In our endeavor we follow the methods of x-ray fluorescence spectroscopy (van Grieken & Markowicz 2001, Beckhoff et al. 2006). We will first derive an expression for the number of photons emitted by *i* as if there was no holographic oscillation in  $\sigma_i$ , i.e., for the time being it is assumed that  $\sigma_i = \sigma_i^0$ . The holographic oscillation will be later introduced by making a set of appropriate substitutions.



Figure 3.1: Matrix effects in XFH. (a) Direct excitation. The incident beam excites element *i*. As it passes through the sample it is absorbed along the red path which is equal to  $x/\cos\theta$ . (b) Indirect excitation. Element *j* is excited by the incident beam and emits fluorescence through the  $\nu$  line. If the energy  $E_{j,\nu}$ , of the emitted fluorescence, is sufficiently high then element *i* is excited indirectly. Both figures, (a) and (b), are complementary with the setup in figure 1.4.

### 3.1.1 Direct excitation

Direct excitation is the simplest excitation process and it is shown in figure 3.1(a). Element *i* is placed in a thin layer inside the sample. It is directly excited by the incident beam. The whole process can be divided into a few steps.

First, the beam enters the sample and is attenuated as it penetrates through it (red part of the arrow). The fraction I of the initial beam's photon flux that reaches the thin layer at depth t is given by the Lambert-Beer law, namely

$$I(E,\theta,t) = I_0(E) e^{-\mu(E)\varrho t/\cos\theta},$$
(3.2)

where  $I_0$  is the initial photon flux (in units photons per second) of the beam and  $\rho$  is the sample's density. The total mass attenuation coefficient of the sample  $\mu$  is given by

$$\mu(E) = \sum_{j} W_{j} \mu_{j}^{0}(E), \qquad (3.3)$$

where  $W_j$  is the weight fraction of element j,  $\mu_j^0$  is the mass attenuation coefficient of element j and the j sum runs over all the elements that constitute the sample.
Second, a fraction of the initial photon flux that reaches the thin layer is absorbed in it. We are interested in absorption only by atoms of type i. The fraction of the photon flux that is absorbed is given by

$$\underline{\rho}dt/(\cos\theta)W_i\sigma^0_{iS}(E),\tag{3.4}$$

where  $\sigma_{iS}^0$  is the partial photoionization cross section of shell S and  $W_i$  is the weight fraction of element i in the sample. In the x-ray energy range the photons from the incident beam mainly interact with atoms in the layer through the photoelectric process. When a photon ejects an electron from the S shell a vacancy is created in the shell. This vacancy is then filled by electrons from higher shells and a fluorescence photon or an Auger electron can be emitted. The fraction of vacancy fillings that will result in an emission of a fluorescence photon is given by the fluorescence yield  $\omega_{iS}$ . The probability that the emitted fluorescence photon will be from the  $\lambda$  line is given by the fractional radiative rate  $F_{i\lambda}$ .

The third and final step of the direct excitation process is the absorption of the outgoing fluorescence photons in the sample. The fraction of the fluorescence photons that will reach the detector is given by the Lambert-Beer exponent, namely  $e^{-\mu(E_{i,\lambda})\varrho t/\cos\theta_0}$ .

The number of photons  $dY_{i,\lambda}^{0,\text{DE}}$  emitted by elements *i* from the layer at depth *t* is then given by a multiplication of all the mentioned terms (De Boer 1990)

$$dY_{i,\lambda}^{0,\mathrm{DE}}(E,\theta,t) = \left[ I_0(E) \mathrm{e}^{-\mu(E)\varrho t/\cos\theta} \frac{\varrho \mathrm{d}t}{\cos\theta} W_i \tau_{i,\lambda}^0(E) \right] \mathrm{e}^{-\mu(E_{i,\lambda})\varrho t/\cos\theta_0} g_{i,\lambda},\tag{3.5}$$

where  $g_{i,\lambda} = d\Omega/(4\pi)\epsilon_{i,\lambda}$  is a detector dependent constant. The detector is assumed to have a solid angle coverage of  $d\Omega$  and a sensitivity to a given energy line given by  $\epsilon_{i,\lambda}$ . In equation (3.5) we have introduced the x-ray fluorescence cross section  $\tau_{i,\lambda}^0$  which is given by (Krause et al. 1978, Schoonjans et al. 2011)

$$\tau_{i,\lambda}^0(E,\theta) = \sigma_{iS}^0(E)\omega_{iS}F_{i\lambda}.$$
(3.6)

To obtain the number of fluorescence photons from the whole sample we have to divide the sample into many layers and add contributions  $dY_{i,\lambda}^{0,\text{DE}}$  from all of them. The division is performed into infinitely many infinitesimally thin layers and the sum is replaced with an integral over the sample's thickness. The number of fluorescence photons  $Y_{i,\lambda}^{0,\text{IE}}$  originating from direct excitation and emitted by atoms of type *i* is given by

$$Y_{i,\lambda}^{0,\mathrm{DE}}(E,\theta) = \int_0^T \frac{g_{i,\lambda} W_i}{\cos \theta} I_0(E) \tau_{i,\lambda}^0(E) \mathrm{e}^{-\mu(E)\varrho t/\cos \theta} \mathrm{e}^{-\mu(E_{i,\lambda})\varrho t/\cos \theta_0} \varrho \,\mathrm{d}t.$$
(3.7)

This integral can be easily calculated and the result is

$$Y_{i,\lambda}^{0,\text{DE}}(E,\theta) = \frac{g_{i,\lambda}}{\cos\theta} W_i \tau_{i,\lambda}^0(E) I_0(E) \frac{1 - e^{-\mu(E,\theta,E_{i,\lambda})\varrho T}}{\widetilde{\mu}(E,\theta,E_{i,\lambda})},$$
(3.8)

where

$$\widetilde{\mu}(E,\theta,E_{i,\lambda}) = \frac{\mu(E)}{\cos\theta} + \frac{\mu(E_{i,\lambda})}{\cos\theta_0}.$$
(3.9)

For thick samples it can be assumed that  $T \to \infty$  and equation (3.8) reduces to

$$Y_{i,\lambda}^{0,\mathrm{DE}}(E,\theta) = \frac{g_{i,\lambda}}{\cos\theta} W_i \tau_{i,\lambda}^0(E) I_0(E) \frac{1}{\widetilde{\mu}(E,\theta,E_{i,\lambda})}.$$
(3.10)

#### 3.1.2 INDIRECT EXCITATION

Apart from the direct excitation process i can be also excited indirectly. Indirect excitation is schematically shown in figure 3.1(b). The incident beam first excites element j which emits fluorescence through the  $\nu$  energy line. If the energy  $E_{j,\nu}$  of the emitted fluorescence is higher than the binding energy of electrons in the shell that corresponds to the  $\lambda$  line then element i can be excited and can emit fluorescence. The two elements involved i and j do not have to be different from one another. Self excitations, via different shells, are not excluded.

To calculate the number of photons originating from IE we proceed in a similar way as for direct excitation. We consider two layers. The first layer is located at  $t_1$  and the second at  $t_2$ . The photon flux of the incident beam at the first layer is reduced according to the Lambert-Beer law and reads  $I_0(E) \exp(-\mu(E)\varrho t_1/\cos\theta)$ . The fraction of photons that are absorbed in the first layer is given by an analogous expression to (3.4), namely  $\varrho dt_1/(\cos\theta)W_j\sigma_{jS}^0(E)$ . Here, however, we are interested in the absorption of the beam by atoms of type j not i. As before we need the fraction of vacancies that will result in fluorescence radiation. This fraction is given by  $\omega_{jS}$ . We also need the probability  $F_{j\nu}$  that photons in the  $\nu$  line will be emitted. The fraction of fluorescence photons emitted by j that will reach the layer at  $t_2$  is  $\exp(-\mu(E_{j,\nu})\varrho|t_1 - t_2|/\sin\alpha)$ . The fluorescence photons present in the  $d\Omega'$  solid angle will be absorbed in the layer at  $t_2$ . The absorbed photons will produce vacancies in the atoms of type i. A fraction  $\omega_{iS}$  of the vacancies will result in fluorescence will be from the  $\lambda$  line is given by  $F_{i\lambda}$ . A fraction  $\exp(-\mu(E_{i,\lambda})\varrho t_2/\cos\theta_0)$  of the emitted fluorescence will reach the detector.

The number of photons  $dY_{i,\lambda}^{0,\text{IE}}$  emitted in an indirect excitation process in which only two layers at fixed depths in the sample are considered is given by

$$dY_{i,\lambda}^{0,\mathrm{IE}} = \left[ I_0(E) \mathrm{e}^{-\mu(E)\varrho t_1/\cos\theta} W_j \tau_{j,\nu}^0(E) \frac{\varrho \mathrm{d}t_1}{\cos\theta} \right] \left[ \frac{\mathrm{d}\Omega'}{4\pi} \mathrm{e}^{-\mu(E_{j,\nu})\varrho |t_1 - t_2|/\sin\alpha} W_i \tau_{i,\lambda}^0(E_{j,\nu}) \frac{\varrho \mathrm{d}t_2}{\sin\alpha} \right] \times \\ \times \mathrm{e}^{-\mu(E_{i,\lambda})\varrho t_2/\cos\theta_0} g_{i,\lambda}.$$
(3.11)

Actually, the two considered layers can be located at different depths inside the sample. To obtain the total number of photons  $Y_{i,\lambda}^{0,\text{IE}}$  originating from IE we have to consider all possible positions of

the two layers. We again assume that the layers are infinitesimally thin and add all contributions from all the possible positions of the layers. In the limit of infinitesimally thin layers the sum is expressed as an integral and reads

$$Y_{i,\lambda}^{0,\mathrm{IE}} = \int_{-\pi/2}^{\pi/2} \int_{0}^{T} \int_{0}^{T} \left[ I_{0}(E) \mathrm{e}^{-\mu(E)\varrho t_{1}/\cos\theta} W_{j} \tau_{j,\nu}^{0}(E) \frac{\varrho}{\cos\theta} \right] \\ \times \left[ \frac{1}{2} \mathrm{e}^{-\mu(E_{j,\nu})\varrho|t_{1}-t_{2}|/\sin\alpha} W_{i} \tau_{i,\lambda}^{0}(E_{j,\nu}) \frac{\varrho}{\sin\alpha} \right] \mathrm{e}^{-\mu(E_{i,\lambda})\varrho t_{2}/\cos\theta_{0}} g_{i,\lambda} \sin\alpha \, \mathrm{d}t_{2} \mathrm{d}t_{1} \mathrm{d}\alpha, \qquad (3.12)$$

where we have put  $d\Omega' = 2\pi \sin \alpha \, d\alpha$ . The  $2\pi$  factor arises because the two elements *i* and *j* do not have to lie in the sample plane as in figure 3.1(b). For finite sample sizes  $(T < \infty)$  the integral in (3.12) is rather cumbersome and the result is rather complicated (van Dyck et al. 1986). Here to keep the discussion simple we will assume that the sample is semi infinite which is a good approximation in many cases.<sup>1</sup> For semi infinite samples  $T \to \infty$  the integral in (3.12) can be evaluated to

$$Y_{i,\lambda}^{0,\mathrm{IE}} = \frac{g_{i,\lambda}}{\cos\theta} \frac{I_0(E)W_iW_j}{\widetilde{\mu}(E,\theta,E_{i,\lambda})} \tau_{j,\nu}^0(E) \tau_{i,\lambda}^0(E_{j,\nu}) \mathcal{L}(E,E_{i,\lambda},E_{j,\nu},\theta), \qquad (3.13)$$

where

$$\mathcal{L}(E, E_{i,\lambda}, E_{j,\nu}, \theta) = \frac{\cos\theta}{2\mu(E)} \ln\left(1 + \frac{\mu(E)}{\mu(E_{j,\nu})\cos\theta}\right) + \frac{\cos\theta_0}{2\mu(E_{i,\lambda})} \ln\left(1 + \frac{\mu(E_{i,\lambda})}{\mu(E_{j,\nu})\cos\theta_0}\right).$$
 (3.14)

Equation (3.13) gives the number of photons from the indirect excitation process but only if i is excited by only one line  $\nu$  and only one other element j. In real systems i might be excited by emission lines from many different elements that make up the sample. For each element there may be many lines that will be able to excite i. Therefore, to obtain the total number of photons emitted by i in the indirect excitation process we have to sum (3.13) over all the lines than can excite i and over their corresponding elements j. This gives the final expression for indirect excitation equal to

$$Y_{i,\lambda}^{0,\mathrm{IE}} = \frac{g_{i,\lambda}}{\cos\theta} \frac{I_0(E)W_i}{\widetilde{\mu}(E,\theta,E_{i,\lambda})} \sum_j \sum_{\nu} W_j \tau_{j,\nu}^0(E) \tau_{i,\lambda}^0(E_{j,\nu}) \mathcal{L}(E,E_{i,\lambda},E_{j,\nu},\theta).$$
(3.15)

#### 3.1.3 The total number of measured photons

To obtain the total number of photons  $Y_{i,\lambda}^0$  that will reach the detector we need to sum equations (3.10) and (3.15). This leads to

$$Y_{i,\lambda}^{0} = \frac{g_{i,\lambda}}{\cos\theta} \frac{W_{i}\tau_{i,\lambda}^{0}(E)I_{0}(E)}{\widetilde{\mu}(E,\theta,E_{i,\lambda})} + \frac{g_{i,\lambda}}{\cos\theta} \frac{I_{0}(E)}{\widetilde{\mu}(E,\theta,E_{i,\lambda})} \sum_{j} \sum_{\nu} W_{i}W_{j}\tau_{j,\nu}^{0}(E)\tau_{i,\lambda}^{0}(E_{j,\nu})\mathcal{L}(E,E_{i,\lambda},E_{j,\nu},\theta).$$
(3.16)

<sup>&</sup>lt;sup>1</sup>The case when the sample's thickness is fixed is discussed by van Dyck et al. (1986). A discussion of matrix effects in XFH for samples of arbitrary thickness was recently considered by Dul & Korecki (2015b).

An equation of this type was first derived by Sherman (1955) and (3.16) is sometimes referred to as the Sherman equation. It can be written in a more convenient form as

$$Y_{i,\lambda}^{0} = \frac{g_{i\lambda}I_{0}(E)W_{i}}{\cos\theta\tilde{\mu}(E, E_{i,\lambda})}\tau_{i,\lambda}^{0}(E)H_{i,\lambda},$$
(3.17)

where

$$H_{i,\lambda} = 1 + \frac{1}{\tau_{i,\lambda}^{0}(E)} \sum_{j,\nu} W_{j} \tau_{i,\lambda}^{0}(E_{j,\nu}) \tau_{j,\nu}^{0}(E) \mathcal{L}(E, E_{i,\lambda}, E_{j,\nu}, \theta).$$
(3.18)

Let us remark that in the derivation of equation (3.17) we have neglected tertiary excitation (Beckhoff et al. 2006). Tertiary excitation is a process like indirect excitation but involves three, not two elements. The incident beam first excites element  $j_1$  which emits fluorescence. This fluorescence then excites element  $j_2$  which also emits fluorescence. Finally, the fluorescence from  $j_2$  excites i which emits the fluorescence that we want to detect. The contribution of tertiary excitation to  $Y_{i,\lambda}^0$  is considered most often to be negligible. For this reason and to keep the discussion simple we neglect tertiary excitation. However, our proceeding discussion is quite general and can be extended to account for tertiary excitation if needed.

# 3.1.4 INTRODUCING THE HOLOGRAPHIC OSCILLATIONS

We have derived equation (3.17) using the methods of x-ray fluorescence spectroscopy. In doing so, we have neglected the holographic oscillations of the photoionization cross sections. To reintroduce them into  $Y_{i,\lambda}^0$  we make the following substitutions in equation (3.17):

$$\tau_{i,\lambda}^{0}(E) \mapsto \tau_{i,\lambda}^{0}(E,\theta,\phi) = \tau_{i,\lambda}^{0}(E)[1 + \chi_{i}(E,\theta,\phi)], \qquad (3.19a)$$

$$\tau_{j,\lambda}^{0}(E) \mapsto \tau_{j,\lambda}^{0}(E,\theta,\phi) = \tau_{j,\lambda}^{0}(E)[1 + \chi_{j}(E,\theta,\phi)], \qquad (3.19b)$$

$$\mu_j^0(E) \mapsto \mu_j^0(E, \theta, \phi) = \mu_j^0(E) [1 + \chi_j(E, \theta, \phi)].$$
(3.19c)

The first two substitutions follow from equations (3.1) and (3.6). The total photoionisation cross section  $\sigma_i^0$  of an isolated atom of kind *i* can be written as (Beckhoff et al. 2006)

$$\sigma_i^0 = \sigma_{i\mathrm{K}}^0 + \sigma_{i\mathrm{L}1}^0 + \sigma_{i\mathrm{L}2}^0 + \dots$$
(3.20)

If the considered atom is part of a larger system of atoms then by means of equation (3.1)  $\sigma_i^0$  needs to be replaced with  $\sigma_i(E, \theta, \phi) = \sigma_i^0(E)[1 + \chi_i(E, \theta, \phi)]$ . Then

$$\sigma_{i} = \sigma_{i}^{0} [1 + \chi_{i}(E, \theta, \phi)] = \underbrace{\sigma_{iK}^{0} [1 + \chi_{i}(E, \theta, \phi)]}_{\sigma_{iK}} + \underbrace{\sigma_{iL1}^{0} [1 + \chi_{i}(E, \theta, \phi)]}_{\sigma_{iL1}} + \dots$$
(3.21)

and we can write

$$\sigma_{iS} = \sigma_{iS}^{0} [1 + \chi_i(E, \theta, \phi)], \qquad (3.22)$$

where  $S \in \{K, L1, L2, ...\}$ . Now if we wish to calculate the x-ray fluorescence cross section of an element that is part of a larger system of atoms,  $\sigma_{iS}^0$  in equation (3.6) needs to be replaced with  $\sigma_{iS}^0[1 + \chi_i(E, \theta, \phi)]$  and one obtains  $\tau_{i,\lambda}^0 = \omega_{iS}F_{i,\lambda}\sigma_{iS}^0[1 + \chi_i(E, \theta, \phi)] = \tau_{i,\lambda}^0[1 + \chi_i(E, \theta, \phi)]$ , i.e., equation (3.19a) and equivalently (3.19b).

The third substitution follows from equation (3.3). The total mass attenuation coefficient of an isolated atom of type j can be written as a sum of the photoionisation  $(\sigma_i^0)$ , elastic  $(\sigma_i^{\rm el})$  and inelastic  $(\sigma_i^{\rm inel})$  cross sections, i.e.,

$$\mu_{j}^{0}(E) = \sigma_{j}^{0}(E) + \sigma_{j}^{\rm el}(E) + \sigma_{j}^{\rm inel}(E).$$
(3.23)

In the x-ray energy range the photoionization cross section dominates over the elastic and nonelastic ones, i.e.,  $\sigma_j^0 \gg \sigma_j^{\text{el}}$  and  $\sigma_j^0 \gg \sigma_j^{\text{inel}}$  and one can approximate  $\mu_j^0 \approx \sigma_j^0$ . Again if element j is part of a system of atoms then  $\sigma_j^0$  needs to be replaced with  $\sigma_j = \sigma_j^0 [1 + \chi_j(E, \theta, \phi)]$ . This yields the third substitution (3.19c).

## 3.1.5 Breakdown of direct proportinality

The number of measured photons  $Y_{i,\lambda}^0$  [equation (3.17)] after the (3.19a), (3.19b) and (3.19c) substitutions will be denoted by  $Y_{i,\lambda}$ . If we analyze the structure of  $Y_{i,\lambda}$  then it becomes evident that, when matrix effects are present,  $Y_{i,\lambda}$  is not directly proportional to  $\sigma_i$ . In fact, owing to the sum over all the sample's elements in  $\mu$  [equation (3.3)]  $Y_{i,\lambda}$  depends on holographic signals of all elements in the sample, not just on  $\chi_i$ ! As a result we cannot use equation (1.25) to obtain  $\chi_i$  from  $Y_{i,\lambda}$ . This is in fact against "common logic" in XFH since equation (1.25) is commonly used to obtain holograms for a given element *i* from the measured number of photons (Hayashi et al. 2012).

# 3.2 EXPANDING $Y_{i,\lambda}$

After the (3.19a), (3.19b) and (3.19c) substitutions it is evident that the relation between  $Y_{I,\lambda}$  and  $\chi_i$  is nonlinear. This makes any kind of analysis of  $Y_{i,\lambda}$  very complicated. To proceed further we take advantage of the fact that the holographic signal is small ( $\chi \sim 10^{-4}$ ) and expand  $Y_{i,\lambda}$  with respect to  $\chi$ . This can be formally written as

$$Y_{i,\lambda} \simeq Y_{i,\lambda}|_{\chi=0} + \sum_{n} \left( \frac{\partial Y_{i,\lambda}}{\partial \chi_{n}} \Big|_{\chi=0} \right) \chi_{n}$$
$$\simeq Y_{i,\lambda}^{0} \times \left[ 1 + \sum_{n} c_{i,n,\lambda} \chi_{n} \right], \qquad (3.24)$$

where  $\chi = 0$  means that the derivative is calculated at zero i.e  $\chi_i = 0$  and  $\chi_j = 0$ . In equation (3.24) we have neglected quadratic and higher terms in  $\chi$ . The *n* sum runs over all the elements in the

sample and

$$Y_{i,\lambda}^{0} = Y_{i,\lambda}\Big|_{\chi=0}$$
 and  $c_{i,n,\lambda} = \frac{1}{Y_{i,\lambda}^{0}} \left(\frac{\partial Y_{i,\lambda}}{\partial \chi_{n}}\Big|_{\chi=0}\right).$  (3.25)

The expansion coefficients  $c_{i,n,\lambda}$  are calculated in the Appendix. They can be conveniently written as a sum of two parts (Dul et al. 2013)

$$c_{i,n,\lambda} = \frac{1}{H_{i,\lambda}} \left( c_{i,n,\lambda}^{\text{BA}} + c_{i,n,\lambda}^{\text{IE}} \right).$$
(3.26)

The first part  $c_{i,n,\lambda}^{BA}$  results from the differentiation of equation (3.10) with respect to  $\chi_n$ . It is responsible for beam attenuation since it originates from the exponential term  $\exp(-\mu(E)\varrho t/\cos\theta)$ in equation (3.5). It is given by

$$c_{i,n,\lambda}^{\mathrm{BA}} = \delta_{in} - \frac{\mu_n^0(E)W_n}{\tilde{\mu}(E,\theta,E_{i,\lambda})\cos\theta},\tag{3.27}$$

where  $\delta_{in}$  is the Kronecker delta symbol.

The second part is a result of the differentiation of equation (3.15) and describes indirect excitation. It is given by

$$c_{i,n,\lambda}^{\mathrm{IE}} = \frac{1}{\tau_{i,\lambda}^{0}} \sum_{j,\nu} W_j \tau_{i,\lambda}^{0} \tau_{j,\nu}^{0} \mathcal{L}(E, E_{i,\lambda}, E_{j,\nu}, \theta) \left( \delta_{jn} - \frac{\mu_n^0(E)W_n}{\tilde{\mu}\cos\theta} + \frac{\mathcal{L}'(E, E_{j,\nu}, \theta)}{\mathcal{L}(E, E_{i,\lambda}, E_{j,\nu}, \theta)} \right), \quad (3.28)$$

where

$$\mathcal{L}'(E, E_{j,\nu}, \theta) = \frac{\mu_n^0(E)W_n}{2\mu(E)} \left[ \frac{1}{\mu(E_{j,\nu})\mathcal{Q}} - \frac{\cos\theta}{\mu(E)} \ln\left(\mathcal{Q}\right) \right]$$
(3.29)

and  $\mathcal{Q} = 1 + \mu(E) / [\mu(E_{j,\nu}) \cos \theta].$ 

### 3.3 HOLOGRAM MIXING

Equation (3.24) is a theoretical relation between the number of photons measured in the detector and the holographic signal or we should rather say holographic signals.

From the experimental point of view we use equation (1.23). Although we are not permitted to use it to obtain  $\chi_i$  we can still use it to obtain the overall holographic oscillation present in the measured number of photons. We rewrite (1.23) as

$$Y_{i,\lambda}^{\exp}(E,\theta,\phi) = Y_{i,\lambda}^{0,\exp}(E,\theta)[1 + \chi_{i,\lambda}^{\exp}(E,\theta,\phi)], \qquad (3.30)$$

where the superscript "exp" explicitly denotes that  $Y_{i,\lambda}^{\text{exp}}$  is the number of photons measured in the experiment. Similarly,  $Y_{i,\lambda}^{0,\text{exp}}$  denotes the slowly varying background that needs to be fitted to  $Y_{i,\lambda}^{\text{exp}}$ 

to obtain the experimental hologram  $\chi_{i,\lambda}^{\exp}$ .  $\chi_{i,\lambda}^{\exp}$  denotes the overall holographic oscillation. Note that we have added a  $\lambda$  index to  $\chi_{i,\lambda}^{\exp}$ .

The measured number of photons  $Y_{i,\lambda}^{exp}$  and the theoretical predicted number of photons  $Y_{i,\lambda}$  should be equal. If we compare the two we obtain (Dul et al. 2013)

$$\chi_{i,\lambda}^{\exp}(E,\theta,\phi) = \sum_{n} c_{i,n,\lambda}(E,\theta)\chi_n(E,\theta,\phi), \qquad (3.31)$$

where in the derivation we have put  $Y_{i,\lambda}^{0,\exp} = Y_{i,\lambda}^0$ . This assumption must hold because in the limit  $\chi_n \to 0$  we should obtain the Sherman equation  $Y_{i,\lambda}^0$ . Equation (3.31) connects the overall holographic signal  $\chi_{i,\lambda}^{\exp}$  which can be obtained from the experiment with the actual holograms  $\chi_n$ .

Equation (3.31) has serious consequences for element sensitive atomic structure imaging with XFH. Normally we would expect that  $\chi_{i,\lambda}^{\exp} = \chi_i$ . In this case, which holds for thin samples,  $\chi_{i,\lambda}^{\exp}$  is element sensitive, i.e., it contains information only about the atomic structure around *i*. However, for thick samples we have in general  $\chi_{i,\lambda}^{\exp} \neq \chi_i$ . The element sensitivity of  $\chi_{i,\lambda}^{\exp}$  is reduced or one can even say that it is lost. The information about  $\chi_i$  is present in  $\chi_{i,\lambda}^{\exp}$  but it is overshadowed by other holograms. In other words  $\chi_{i,\lambda}^{\exp}$  contains not only information about the surrounding of *i*, but also information about the surrounding of all other elements that significantly contribute to the total absorption coefficient of the sample. We can colloquially say that the hologram obtained from the experiment is a "mixture" of all the "pure" holograms  $\chi_n$ . The reduction of element sensitivity cannot be ignored as it can make the data analysis and structure determination with XFH ambiguous.

# 3.4 Properties of $c_{i,n,\lambda}$

Of course whether  $\chi_{i,\lambda}^{\exp}$  will be element sensitive or not, how big will the element sensitivity reduction be, is determined by the values of the  $c_{i,n,\lambda}$  coefficients. These are given only by fundamental parameters such absorption cross sections and weight fractions of elements in the sample. They are independent of the parameters used in the experiments, e.g., the beam flux, the detector's sensitivity to a given energy line or its solid angle coverage.

To show the possible magnitude of element sensitivity reduction let us consider an example of Cu<sub>3</sub>Au. Cu<sub>3</sub>Au can be considered as a model system in XFH. It was used in the pioneering experiments by Adams et al. (1998) and it was also used to study extinction effects in XFH (Korecki, Novikov, Tolkiehn & Materlik 2004). The ordered phase of Cu<sub>3</sub>Au has a simple facecentered cubic structure with a lattice constant equal to a = 3.753 Å and the Pm3m space group. The Cu<sub>3</sub>Au structure is schematically drawn in figure 3.2(a). The conventional unit cell for this structure is marked with the white lines that form a cube. The gold atoms are located at the corners of the unit cell while the copper atoms are located at the centers of the faces. From the point of view of XFH, it is important to note that the gold atoms occupy a single crystallographically

#### 3. MATRIX EFFECTS IN MONOCHROMATIC XFH

equivalent position in the unit cell. For the copper atoms one can distinguish three nonequivalent positions. These are labeled in figure 3.2(a) as  $Cu_1$ ,  $Cu_2$  and  $Cu_3$ . This means that there are three copper detectors and the copper hologram will be an average of holograms detected by each of these detectors. Let us stop here for a moment and discuss what kind of structure we expect to obtain when reconstructing a copper hologram. We will need this information later in the text.



Figure 3.2:  $Cu_3Au$  structure. (a) The  $Cu_3Au$  structure with marked four cubes in color. (b) The four color cubes shown separately. (c) A unit cell that one expects to reconstruct from the copper holograms. At the centers of the walls of the cube the odd looking electron density Au/3 + 2Cu/3 is expected and is a direct consequence of the three copper detectors  $Cu_1$ ,  $Cu_2$  and  $Cu_3$ . (d) A unit cell that one expects to obtain form the reconstruction of a gold hologram.

Apart from the conventional unit cell there are three additional cubes marked in figure 3.2(a). These other cubes are marked in different colors (red, green and blue). These cubes can be obtained through translation of the white cube that marks the unit cell. If we take the labeled gold atom as the origin (0, 0, 0) and shift the white cube by (0.5a, 0.5a, 0.0) we obtain the blue cube. To obtain the green cube we have to shift the white cube by (0.0, 0.5a, 0.5a). To get the red cube we shift the

white one by (0.5a, 0.0, 0.5a). Each of the colored cubes is then anchored at one of the nonequivalent copper sites Cu<sub>1</sub>, Cu<sub>2</sub> or Cu<sub>3</sub>. In figure 3.2(b) we plot each cube separately and explicitly mark the positions of the three detector atoms Cu<sub>1</sub>, Cu<sub>2</sub> and Cu<sub>3</sub>. The cubes are all oriented in the same direction. The red, blue and green cubes show part of the Cu<sub>3</sub>Au structure that is perceived by each of the copper detector atoms. The structure that we expect to obtain from a copper hologram is, thus, an average over the red, blue and green cubes. At the corners, these cubes have copper atoms. When reconstructing a copper hologram we expect to obtain a copper atom in these positions. At the faces there are always two copper atoms and one gold atom. Therefore, at the faces we expect to obtain an averaged electron density, namely Au/3 + 2Cu/3. The resulting structure that is expected from a copper hologram is shown in figure 3.2(c). For completeness, in figure 3.2(d) we depict the structure that is expected from the reconstruction of a gold hologram. It is the conventional unit cell of Cu<sub>3</sub>Au, since as mentioned before, gold atoms occupy a single crystallographically equivalent position.

After this structure digression we return back to the properties of the  $c_{i,n,\lambda}$  coefficients. We assume that two holograms are measured, one copper hologram  $\chi_{Cu,K\alpha}^{exp}$  with K $\alpha$  radiation and one gold hologram  $\chi_{Au,L\alpha}^{exp}$  with L $\alpha$  radiation. The copper K edge lies at 8.99 keV whereas the L lines of gold have energies  $E_{Au,L\alpha} = 9.70$  keV and  $E_{Au,L\beta} = 11.47$  keV. Therefore, the copper atoms can be indirectly excited by fluorescence from gold atoms if the incident beam energy is higher then the energy of the gold  $L_3$  edge which is equal to 11.92 keV. Gold L $\alpha$  fluorescence cannot be induced by copper fluorescence and so in this particular case gold atoms cannot be indirectly excited. The "mixing" equations for the  $\chi_{Cu,K\alpha}^{exp}$  and  $\chi_{Au,L\alpha}^{exp}$  holograms given by (3.31) and can be written in matrix form as

$$\begin{pmatrix} \chi_{Au,L\alpha}^{exp} \\ \chi_{Cu,K\alpha}^{exp} \end{pmatrix} = \underbrace{\begin{pmatrix} c_{Au,Au,L\alpha} & c_{Au,Cu,L\alpha} \\ c_{Cu,Au,K\alpha} & c_{Cu,Cu,K\alpha} \end{pmatrix}}_{\mathbf{C}} \begin{pmatrix} \chi_{Au} \\ \chi_{Cu} \end{pmatrix}.$$
(3.32)

There are four  $c_{i,n,\lambda}$  coefficients in this example and they make up the **C** matrix which we can colloquially term as the "mixing matrix". The  $c_{i,n,\lambda}$  coefficients from (3.32) are plotted in figure 3.3 as a function of the incident beam energy E and  $\theta$ . To calculate the relevant cross sections in  $c_{i,n,\lambda}$ we have used the *xraylib* library (Schoonjans et al. 2011). We have also aligned the detector with the surface normal by setting  $\theta_0 = 0^\circ$ . In the absence of matrix effects the  $c_{i,n,\lambda}$  coefficients should be equal to  $c_{i,n,\lambda} = \delta_{in}$ . The **C** matrix should be an identity matrix  $\mathbf{C} = \mathbf{1}$ . For thick samples this is not the case. In general, we have  $c_{i,n,\lambda} \neq \delta_{in}$ .

Consider first  $c_{Au,Au,L\alpha}$  and  $c_{Au,Cu,L\alpha}$ . For these coefficients only the beam attenuation part  $c_{i,n,\lambda}^{BA}$  of  $c_{i,n,\lambda}$  is relevant. There is no indirect excitation and  $H_{i,\lambda} = 1$  and  $c_{i,n,\lambda}^{IE} = 0$ . In the absence of IE it follows from equation (3.27) that if i = n then  $0 < c_{i,n,\lambda} < 1$  and if  $i \neq n$  then  $c_{i,n,\lambda} < 0$ . This is because the term  $\mu_n^0 W_n / (\tilde{\mu}(E, \theta, E_{i,\lambda}) \cos \theta)$  in  $c_{i,n,\lambda}^{BA}$  is always less then one. This behavior



Figure 3.3: Example  $c_{i,n,\lambda}$  coefficients for Cu<sub>3</sub>Au. The  $\theta$  range is from 0° to 89°.

of  $c_{i,n,\lambda}$  can be seen in figures 3.3(a) and 3.3(b). The value of the  $c_{Au,Au,L\alpha}$  coefficient is indeed less then one in the whole  $\theta - E$  plane. Its values approach 1 for higher energies and small  $\theta$  angles. With increasing  $\theta$  the value of  $c_{Au,Au,L\alpha}$  drops.  $c_{Au,Cu,L\alpha}$  is negative in the whole  $\theta - E$  plane.

The behavior of  $c_{\mathrm{Cu},n,\mathrm{K}\alpha}$  is much more complicated than  $c_{\mathrm{Au},n,\mathrm{L}\alpha}$ .  $c_{\mathrm{Cu},\mathrm{Au},\mathrm{K}\alpha}$  and  $c_{\mathrm{Cu},\mathrm{Cu},\mathrm{K}\alpha}$ are plotted in figures 3.3(c) and 3.3(d), respectively. The most eye catching features of the two coefficients are the sharp discontinuities in the energy range. The discontinuities appear exactly at the energies of the *L* edges of gold. When the beam energy increases above a certain edge and the absorption cross sections experience a jump, the copper atoms can be excited by fluorescence photons from gold and this is manifested in  $c_{i,n,\lambda}$ . Both contributions  $c_{i,n,\lambda}^{\mathrm{BA}}$  and  $c_{i,n,\lambda}^{\mathrm{IE}}$  experience such jumps. The BA contribution  $c_{\mathrm{Cu},n,\mathrm{K}\alpha}^{\mathrm{BA}}$  is plotted in figures 3.3(e) and 3.3(f). We see that despite the sharp discontinuities  $0 < c_{\mathrm{Cu},\mathrm{Cu},\mathrm{K}\alpha}^{\mathrm{BA}} < 1$  and  $c_{\mathrm{Cu},\mathrm{Au},\mathrm{K}\alpha}^{\mathrm{BA}} < 0$  which is in agreement with the discussion for  $c_{\mathrm{Au},n,\mathrm{K}\alpha}^{\mathrm{BA}}$ . The IE contribution  $c_{\mathrm{Cu},n,\mathrm{L}\alpha}^{\mathrm{IE}}$  is plotted in figures 3.3(g) and 3.3(h). For beam energies which are lower then the  $L_1$  gold edge the IE contributions are equal to zero because IE is not possible. It is difficult to draw any general conclusions about the signs and bounds of  $c_{i,n,\lambda}^{\mathrm{IE}}$ since their structure is rather complicated. From the numerical calculations we can just say that throughout the  $\theta - E$  range  $c_{\mathrm{Cu},\mathrm{Cu},\mathrm{K}\alpha}^{\mathrm{IE}} < 0$  and  $c_{\mathrm{Cu},\mathrm{Cu},\mathrm{K}\alpha}^{\mathrm{IE}} > 0$ .

A nice analogy can be drawn between the impact of matrix effects on XFH and the impact of self-absorption on XAFS spectra. First of all, from figure 3.3 and from the properties of  $c_{i,n,\lambda}$  we can conclude that the amplitude of  $\chi_{i,\lambda}^{exp}$  is lower than  $\chi_i$  (the  $c_{i,i,\lambda}$  coefficients are lower that one). This is exactly analogous to the decrease of the amplitude of XAFS spectra due to self-absorption (Tröger et al. 1992, Pfalzer et al. 1999). In both XFH and XAFS the decrease originates from the attenuation of the x-ray beam inside the sample. In XAFS the decrease can affect the physical parameters that one attempts of obtain from the XAFS spectra. Therefore, in XFH we also expect distortions in the reconstruction of atomic structure which will be related to the lower then expected amplitude of the experimental hologram. Secondly, from equation (3.31) we know that the measured hologram is always a weighted sum of the pure holograms, a phenomenon that we termed "hologram mixing". This is in analogy with the overlap of XAFS oscillations for absorption edges that lie close to one another. When the XAFS oscillations overlap one measures their sum rather than an oscillation from a particular edge. Unlike the XAFS oscillation which fades away very quickly after the absorption edge, the holographic oscillation of the photoionisation cross section extends throughout the energy range and the holographic oscillations always overlap. For proper analysis of XAFS spectra the overlap has to be either modeled (Wende et al. 1998) or the overlapping signals have to be separated (Menard et al. 2009). Otherwise, obtaining valuable structure information from the XAFS spectra is hardly possible and indicates that the same problem is present in XFH.

## 3.5 Impact of matrix effects on structure reconstruction

We now focus on the impact of matrix effects on atomic structure reconstruction. Currently, the most widely used reconstruction algorithm in XFH is the one proposed by Barton (1988, 1991). It was described in Section 1.5 in the Introduction Chapter. The reconstruction is based on equation (1.29). If we insert  $\chi_{i,\lambda}^{\exp}$  into equation (1.29) we obtain

$$U_{i,\lambda}^{\exp}(\mathbf{r}) = \int \chi_{i,\lambda}^{\exp}(\mathbf{k}) e^{-i(kr+\mathbf{k}\cdot\mathbf{r})} d^{3}\mathbf{k}$$
  
$$= \sum_{n} \int c_{i,n,\lambda}(\mathbf{k}) \chi_{n}(\mathbf{k}) e^{-i(kr+\mathbf{k}\cdot\mathbf{r})} d^{3}\mathbf{k}$$
  
$$= \sum_{n} \widetilde{U}_{n,\lambda}(\mathbf{r}), \qquad (3.33)$$

where  $\widetilde{U}_{\lambda,n}(\mathbf{r}) = \int c_{i,n,\lambda}(\mathbf{k})\chi_n(\mathbf{k})e^{-i(kr+\mathbf{k}\cdot\mathbf{r})}d^3\mathbf{k}$  and  $U_{i,\lambda}^{exp}$  is the reconstruction image which we expect to obtain from  $\chi_{i,\lambda}^{exp}$ . In the second line of (3.33) we have used equation (3.31) and changed the order of summation and integration.

The interpretation of equation (3.33) is straightforward. In the absence of matrix effects  $(c_{i,n,\lambda} = \delta_{in})$  we have  $U_{i,\lambda}^{\exp} = U_i$ . The reconstruction image obtained from  $\chi_{i,\lambda}^{\exp}$  resembles the structure around i. In the presence of matrix effects the reconstruction image resembles not only the structure around i but also the structure around other elements. On the right hand side of (3.33) we have a sum of the reconstruction images  $\tilde{U}_{n,\lambda}$ . Each  $\tilde{U}_{n,\lambda}$  reconstruction image contains information solely about the structure around n. Their amplitude depends on the magnitude of  $c_{i,n,\lambda}$ . Thus, in  $U_{i,\lambda}^{\exp}$  we will have a number of maxima that we will be able to attribute to signals from atoms that are in the vicinity of i. Apart from these true maxima there will also be a number of others which we will not be able to assign to signals from atoms from the vicinity of i. Put simply, additional spurious maxima might appear in  $U_{i,\lambda}^{\exp}$  that originate from holograms other than  $\chi_i$  and they might be misinterpreted as signals from actual atoms. Moreover, if the  $c_{i,n,\lambda}$  coefficients have different signs then when summing  $\tilde{U}_{n,\lambda}$  the spurious maxima might cancel the true ones out. This would happen if two elements in the sample would have the same or partly the same local atomic structures (the positions of some atoms around i and another element would coincide).

The problem of distorted reconstruction images due to matrix effect concerns other reconstruction schemes as well. Consider, for example, equation (1.13) with which one can extract structure factors from the holograms. If we start from equation (3.31) and decompose  $\chi_{i,\lambda}^{\exp}$  according to (1.13) we

obtain

$$\chi_{i,\lambda}^{\exp}(\mathbf{k}) = \sum_{n} c_{i,n,\lambda}(\mathbf{k})\chi_{n}(\mathbf{k})$$
$$= -\frac{8\pi r_{e}}{V} \operatorname{Re} \sum_{n} c_{i,n,\lambda}(\mathbf{k}) \sum_{\mathbf{H}} F_{n\mathbf{H}}[\chi_{\mathbf{H}}^{R}(\mathbf{k}) + i\chi_{\mathbf{H}}^{I}(\mathbf{k})]$$
$$= -\frac{8\pi r_{e}}{V} \operatorname{Re} \sum_{\mathbf{H}} F_{i\lambda\mathbf{H}}(\mathbf{k})[\chi_{\mathbf{H}}^{R}(\mathbf{k}) + i\chi_{\mathbf{H}}^{I}(\mathbf{k})], \qquad (3.34)$$

where  $F_{i\lambda\mathbf{H}}(\mathbf{k}) = \sum_{n} c_{i,n,\lambda}(\mathbf{k}) F_{n\mathbf{H}}$ . The structure of equation (3.34) is the same as (1.13) but instead of the structure factors  $F_{i\mathbf{H}}$  that would correspond to i as a detector atom we obtain  $F_{i\lambda\mathbf{H}}$ . If we try to use  $\chi^{R}_{\mathbf{H}}$  and  $\chi^{I}_{\mathbf{H}}$  as basis functions for fitting procedures we will obtain an averaged value of  $F_{i\lambda\mathbf{H}}$  instead of  $F_{i\mathbf{H}}$ . The averaged value differs from the actual structure factors  $F_{i\lambda\mathbf{H}} \neq F_{i\mathbf{H}}$  and will yield a distorted electron density if used for reconstruction.

Of course, the magnitude of the distortions which appear in the reconstruction images in the considered reconstruction schemes will depend on the values of the  $c_{i,n,\lambda}$  coefficients. There might be cases in which they will not pose any significant danger, for example when  $c_{i,i,\lambda} \gg c_{i,n,\lambda}$  for  $i \neq n$ . In general, however, to tackle the distortions a procedure which would allow to correct for matrix effects in XFH is desired. Otherwise any kind of atomic structure determination with XFH might be seriously hindered.

# 3.6 Correcting for matrix effects

As shown in the previous sections, the fact that the  $c_{i,n,\lambda}$  coefficients are not equal to their ideal values  $(c_{i,n,\lambda} = \delta_{in})$  prohibits, in general, element sensitive analysis of atomic structure with XFH. This prospect might seem daunting for anyone who deals with XFH. Fortunately, element sensitivity of  $\chi_{i,\lambda}^{\exp}$  can be restored, i.e.,  $\chi_{i,\lambda}^{\exp}$  can be corrected for matrix effects. The correction is entirely based on equation (3.31).

In general, holograms can be measured for different elements  $(i_1, i_2, ..., i_N)$  in the sample, different energy lines  $(\lambda_1, \lambda_2, ..., \lambda_M)$  and even different  $\theta_0$  angles. If more than one hologram is measured then equation (3.31) can be used to build a set of equations. The most general form of such a set is given by

$$\vec{\chi}_{i,\lambda}^{\exp} = \mathbf{C}\vec{\chi},\tag{3.35}$$

where  $\vec{\chi}_{i,\lambda}^{\exp} = \left(\chi_{i_1,\lambda_1}^{\exp}, \chi_{i_1,\lambda_2}^{\exp}, \chi_{i_2,\lambda_1}^{\exp}, ..., \chi_{i_N,\lambda_M}^{\exp}\right)^{\mathrm{T}}$  is the vector of the measured holograms, the "pure" holograms are contained in  $\vec{\chi} = (\chi_{i_1}, \chi_{i_2}, ..., \chi_{i_N})^{\mathrm{T}}$  and the **C** matrix contains the  $c_{i,n,\lambda}$  coefficients. In the expression for  $\vec{\chi}_{i,\lambda}^{\exp}$  we have intentionally omitted the  $\theta_0$  dependence of the  $\chi_{i,\lambda}^{\exp}$  holograms to keep the expression compact. To correct for matrix effects one has to solve equation (3.35) for  $\vec{\chi}$ .

It needs to be noted that there is no guarantee that (3.35) will have a solution although it can be easily made overdetermined by measuring more holograms then there are elements in the sample. The resulting system of equations might be ill-defined prohibiting any solution.

We have already seen an example of a set of equations that had a form of (3.35). It was the Cu<sub>3</sub>Au example given by equation (3.32). If the two holograms on the left hand side,  $\chi^{exp}_{Au,L\alpha}$  and  $\chi^{exp}_{Cu,K\alpha}$ , would be actually measured then the set of equations (3.32) would be well defined. This follows from the values of the  $c_{i,n,\lambda}$  coefficients in figure 3.3 and can be supported if we calculate the condition number (Cheney & Kincaid 2008) of **C**. The condition number of a matrix basically tells us how sensitive is our solution ( $\chi_{Au}, \chi_{Cu}$ )<sup>T</sup> to a small change in the input ( $\chi^{exp}_{Au,L\alpha}, \chi^{exp}_{Cu,K\alpha}$ )<sup>T</sup>. For our equation this small change is represented by noise and measurement uncertainties. If the condition number is small then a system of linear equations is well defined. If it is large then it is ill-defined. A linear system of equations is said to be well defined if the condition number is not significantly greater than one. The condition number of our example **C** matrix, for the considered  $\theta$  and energy range, is shown in figure 3.4(a). In a wide  $\theta$  range the condition number of **C** is below 5. It is only for grazing angles than the condition number starts to grow rapidly. With the increase of energy the condition number decreases. These values of the condition number imply that in a wide  $\theta - E$  range the system in (3.32) is well defined.

To highlight the possible unsolvability issues of equation (3.35) consider for example the case when only  $\chi^{\exp}_{Cu,K\alpha}$  and  $\chi^{\exp}_{Cu,K\beta}$  are measured. Equation (3.35) then reads

$$\begin{pmatrix} \chi_{\mathrm{Cu},\mathrm{K\alpha}}^{\mathrm{exp}} \\ \chi_{\mathrm{Cu},\mathrm{K\beta}}^{\mathrm{exp}} \end{pmatrix} = \underbrace{\begin{pmatrix} c_{\mathrm{Cu},\mathrm{Cu},\mathrm{K\alpha}} & c_{\mathrm{Au},\mathrm{Cu},\mathrm{K\alpha}} \\ c_{\mathrm{Cu},\mathrm{Cu},\mathrm{K\beta}} & c_{\mathrm{Au},\mathrm{Cu},\mathrm{K\beta}} \end{pmatrix}}_{\mathbf{C}} \begin{pmatrix} \chi_{\mathrm{Au}} \\ \chi_{\mathrm{Cu}} \end{pmatrix}.$$
(3.36)

Interestingly, although no gold fluorescence would be measured the information about  $\chi_{Au}$  is contained in  $\chi_{Cu,K\alpha}^{\exp}$  and  $\chi_{Cu,K\beta}^{\exp}$ . If equation (3.36) could be solved then  $\chi_{Au}$  could be retrieved from the measured holograms. In real circumstances this is very difficult since this system of equations can be regarded as ill-defined. The condition number for the **C** matrix in equation (3.36) is presented in figure 3.4(b). The condition number is larger than 30 throughout the  $\theta - E$  range. Although, technically, equation (3.36) can be solved, i.e., the **C** matrix can be inverted, the solution is sensitive, in the whole  $\theta - E$  range, to small changes in the input data. This means that the input holograms would have to be measured with unprecedented accuracy, i.e., with a very high signal-to-noise ratio.

### More than one energy line

If for a given element, fluorescence from a number of lines  $\lambda_1$ ,  $\lambda_2$ , ...,  $\lambda_N$  (e.g.,  $\lambda_1 = K\alpha$ ,  $\lambda_2 = L\alpha$ , etc.) is measured than it often pays off to sum the measured fluorescence signals  $Y_{i,\lambda_1}$ ,  $Y_{i,\lambda_2}$ , ...,  $Y_{i,\lambda_N}$ . This enhances the signal and gives better quality holograms. In such a situation it is also



Figure 3.4: (a) Condition numbers as a function of  $\theta$  and energy calculated for the 2 × 2 matrices in equation (3.32). (b) is the same as (a) but for equation (3.36).

possible to correct the resulting holograms for matrix effects. To do so we write the total number of measured fluorescence photons  $Y_i$  from element i as

$$Y_{i} = \sum_{a=1}^{N} Y_{i,\lambda_{a}}$$

$$= Y_{i,\lambda_{1}}^{0} \left[ 1 + \sum_{n} c_{i,n,\lambda_{1}} \chi_{n} \right] + Y_{i,\lambda_{2}}^{0} \left[ 1 + \sum_{n} c_{i,n,\lambda_{2}} \chi_{n} \right] + \dots + Y_{i,\lambda_{N}}^{0} \left[ 1 + \sum_{n} c_{i,n,\lambda_{N}} \chi_{n} \right]$$

$$= Y_{i,\lambda_{1}}^{0} + \sum_{n} Y_{i,\lambda_{1}}^{0} c_{i,n,\lambda_{1}} \chi_{n} + Y_{i,\lambda_{2}}^{0} + \sum_{n} Y_{i,\lambda_{2}}^{0} c_{i,n,\lambda_{2}} \chi_{n} + \dots + Y_{i,\lambda_{N}}^{0} + \sum_{n} Y_{i,\lambda_{N}}^{0} c_{i,n,\lambda_{N}} \chi_{n}$$

$$= \sum_{a=1}^{N} Y_{i,\lambda_{a}}^{0} + \sum_{n} \left( \sum_{a=1}^{N} Y_{i,\lambda_{a}}^{0} c_{i,n,\lambda_{a}} \right) \chi_{n}$$

$$= Y_{i}^{0} \left[ 1 + \sum_{n} c_{i,n} \chi_{n} \right], \qquad (3.37)$$

where in the second line we have used equation (3.24) and in the last defined

$$Y_i^0 = \sum_{a=1}^N Y_{i,\lambda_a}^0$$
(3.38)

and

$$c_{i,n} = \left(\sum_{a=1}^{N} Y_{i,\lambda_a}^0 c_{i,n,\lambda_a}\right) / Y_i^0.$$
(3.39)

Equation (3.37) has the same from as (3.24). The only difference is that  $c_{i,n,\lambda}$  are redefined. The new redefined  $c_{i,n}$  coefficients are given by a weighted arithmetic mean of  $c_{i,n,\lambda}$  with  $Y_{i,\lambda}^0$  as the weights. In needs to be noted that the redefined coefficients  $c_{i,n}$  start to depend on the sensitivity of the detector to a given energy line  $\epsilon_{i,\lambda}$ . Other instrumental parameters like the beam flux or detector solid angle coverage cancel out in (3.39).

When the measured fluorescence is summed then, in the experiment, the hologram is retrieved according to

$$Y_i^{\exp} = Y_i^{0,\exp}[1 + \chi_i^{\exp}], \qquad (3.40)$$

where

$$Y_i^{0,\exp} = \sum_{a=1}^N Y_{i,\lambda_a}^{0,\exp} \quad \text{and} \quad \chi_i^{\exp} = \sum_{a=1}^N \chi_{i,\lambda_a}^{\exp}.$$
(3.41)

Equation (3.40) can be derived in a similar way as equation (3.37) by calculating  $Y_i^{\text{exp}} = \sum_{a=1}^N Y_{i,\lambda_a}^{\text{exp}}$ and using (3.30) to represent  $Y_{i,\lambda_a}^{\text{exp}}$ .

If we now compare the right hand sides of equations (3.40) and (3.37) we obtain

$$\chi_i^{\exp}(E,\theta,\phi) = \sum_n c_{i,n}(E,\theta)\chi_n(E,\theta,\phi).$$
(3.42)

Thus, our original "hologram mixing equation" (3.31) preserves its form but the  $c_{i,n,\lambda}$  coefficients are replaced with  $c_{i,n}$ . In an analogous way as we did with equation (3.31) we can use equation (3.42) to build a system of equations that has the same form as (3.35). The only difference now is that  $\bar{\chi}_{i,\lambda}^{exp}$  contains  $\chi_i^{exp}$  instead of  $\chi_{i,\lambda}^{exp}$  and the elements of the **C** matrix are given by  $c_{i,n}$ .

Consider once again the example of Cu<sub>3</sub>Au. Suppose that for gold we measure L $\alpha$  and L $\beta$  fluorescence, i.e.,  $Y_{Au,L\alpha}^{exp}$  and  $Y_{Au,L\beta}^{exp}$ . Similarly for copper we measure K $\alpha$  and K $\beta$  fluorescence, i.e.,  $Y_{Cu,K\alpha}^{exp}$  and  $Y_{Cu,K\beta}^{exp}$ . Then to enhance the statistics we sum the measured fluorescence for gold  $Y_{Au}^{exp} = Y_{Au,L\alpha}^{exp} + Y_{Cu,K\beta}^{exp}$  and for copper  $Y_{Cu}^{exp} = Y_{Cu,K\alpha}^{exp} + Y_{Cu,K\beta}^{exp}$ . Two holograms  $\chi_{Au}^{exp}$  and  $\chi_{Cu}^{exp}$  can be obtained from the sums and equation (3.35) can be written as

$$\begin{pmatrix} \chi_{Au}^{exp} \\ \chi_{Cu}^{exp} \end{pmatrix} = \underbrace{\begin{pmatrix} c_{Au,Au} & c_{Au,Cu} \\ c_{Cu,Au} & c_{Cu,Cu} \end{pmatrix}}_{\mathbf{C}} \begin{pmatrix} \chi_{Au} \\ \chi_{Cu} \end{pmatrix}, \qquad (3.43)$$

where the elements of the C matrix are given by (3.39), e.g.,

$$c_{\rm Cu,Cu} = \frac{Y_{\rm Cu,K\alpha}^{0} c_{\rm Cu,Cu,K\alpha} + Y_{\rm Cu,K\beta}^{0} c_{\rm Cu,Cu,K\beta}}{Y_{\rm Cu,K\alpha}^{0} + Y_{\rm Cu,K\beta}^{0}}.$$
(3.44)

The redefined  $c_{i,n}$  coefficients from equation (3.43) are plotted in figure 3.5(a). To calculate them we have assumed that the detector sensitivity  $\epsilon_{i,\lambda}$  is equal to  $\epsilon_{i,\lambda} = 1$ . The condition number as a function of  $\theta$  for the **C** matrix is plotted in figure 3.5(b). The values are relatively low and, thus, equation (3.43) can be considered as a well-defined system of linear equations.



Figure 3.5: (a) The **C** matrix coefficients from equation (3.43) for E = 17.44 keV. (b) the corresponding condition numbers.

### 3.7 EXPERIMENTAL VALIDATION

We would now like to apply the formalism that we have developed in the previous Sections to real experimental data. For this purpose we will use holograms measured for gold and copper atoms in  $Cu_3Au$ . The data were provided by the author's coworker Karol Dąbrowski. Since the author did not take active part in the measurements and data processing procedures only a short description of the experimental setup will be given. A detail description of the experimental setup can be found in Dabrowski & Korecki (2012) and in Dul et al. (2013). The experimental setup was complimentary with the one that we have adopted in Section 1.3, figure 1.4. Only the used x-ray source and optics require comment. The x-rays were produced by an x-ray tube (50 W, molybdenum anode) and were collimated with polycapillary optics. The collimated beam was monochromatized with a HOPG

crystal. The energy of the monochromatized beam was E = 17.44 keV, i.e., the molybdenum K $\alpha$  radiation. The divergence of the beam was  $0.15^{\circ}$  and limited the angular resolution with which the holograms could be measured.

The sample that was used in the experiment was a commercially available Cu<sub>3</sub>Au single crystal in the ordered phase with a (001) orientation. It had a shape of a cylinder with 10 mm of diameter and 1 mm of thickness. In the measurement process x-ray fluorescence from gold (L $\alpha$  and L $\beta$ ) and copper  $(K\alpha \text{ and } K\beta)$  atoms was collected with a silicon drift detector. The position of the detector was fixed at  $\theta_0 = 0^\circ$ . In the  $\theta$  direction the fluorescence was measured from 26° to 80° in 0.5° steps. In the  $\phi$  direction a full 360° scan was made with 0.15° steps. The total measurement time was 90 hours. The collected photon counts were dead time corrected. In the end, four fluorescence  $\theta - \phi$  scans were obtained two for gold  $Y_{Au,L\alpha}^{exp}(\theta,\phi)$ ,  $Y_{Au,L\beta}^{exp}(\theta,\phi)$  and two for copper  $Y_{Cu,K\alpha}^{exp}(\theta,\phi)$ ,  $Y_{Cu,K\beta}^{exp}(\theta,\phi)$ fluorescence. In principle, four holograms could have been obtained from these four fluorescence  $\theta - \phi$  scans. However, owing to the relatively small count rate of the used energy resolving detector it was better to first add the collected fluorescence photon counts to enhance the statistics, namely  $Y_{\mathrm{Au}}^{\mathrm{exp}}(\theta,\phi) = Y_{\mathrm{Au},\mathrm{L}\alpha}^{\mathrm{exp}}(\theta,\phi) + Y_{\mathrm{Au},\mathrm{L}\beta}^{\mathrm{exp}}(\theta,\phi) \text{ and } Y_{\mathrm{Cu}}^{\mathrm{exp}}(\theta,\phi) = Y_{\mathrm{Cu},\mathrm{K}\alpha}^{\mathrm{exp}}(\theta,\phi) + Y_{\mathrm{Cu},\mathrm{K}\beta}^{\mathrm{exp}}(\theta,\phi).$  Then the gold and copper holograms were obtained from the summed photon counts according to equation (3.40). The obtained gold  $(\chi_{Au}^{exp})$  and copper  $(\chi_{Cu}^{exp})$  holograms where then symmetrized with respect to the  $m\bar{3}m$  point group. The symmetrized holograms are presented in figure 3.6(a). The small empty squares (missing data regions), in the middle and at the edges of the holograms, appear because the holograms were measured in a limited  $\theta - \phi$  range which did not allow to extend the hologram to a full sphere.

The  $\chi_{Au}^{exp}$  and  $\chi_{Cu}^{exp}$  holograms from figure 3.6(a) were corrected from matrix effect. Equation (3.43) was used for the correction. It was solved by calculating the inverse  $\mathbf{C}^{-1}$ . The corrected  $\chi_{Au}$  and  $\chi_{Cu}$  holograms are shown in figure 3.6(b).

For comparison we have also simulated two holograms without matrix effects. The simulations were carried out in reciprocal space with equation (1.16) for reciprocal vectors up to  $|\mathbf{H}| \leq 5 \times 2\pi/a$ . All other parameters of the simulation were set in accordance with the experimental setup. The simulated holograms without matrix effects were then substituted into equation (3.43) to obtain two simulated holograms with matrix effects. The simulated holograms with matrix effects are shown in figure 3.6(c) whereas the simulated holograms without matrix effects are shown in figure 3.6(d).

For the simulations we needed the  $\Gamma$  parameter from equation (1.14). This parameter was determined from the experimental holograms by fitting the profile  $\chi_{\mathbf{H}}^+$  to the Kossel lines that correspond to  $\mathbf{H} = (2\pi/a) \times (1, 1, 1)$ . From here on, we assume that  $\mathbf{H}$  is a reciprocal vector in a cubic system. The projection of the (111) plane is marked with a solid line in figure 3.6(a) for  $\chi_{Cu}^{\exp}$ . The profile along the great dashed circle will be denoted with  $p_{(111)}$ . The  $\Delta \alpha$  variable will be used to measure the distance along  $p_{(111)}$ . We are only interested in the vicinity of  $\Delta \alpha = 0^{\circ}$ . The  $p_{(111)}$  profiles are shown in figure 3.7. The profiles have be averaged over the greater circle determined by the



Figure 3.6: Measured and computer simulated Cu<sub>3</sub>Au holograms. (a) Measured Cu<sub>3</sub>Au holograms  $\chi_{Au}^{exp}$  and  $\chi_{Cu}^{exp}$ . (b) Holograms from (a) corrected for matrix effects. (c) Computer simulated Cu<sub>3</sub>Au holograms with matrix effects. (d) Computer simulated Cu<sub>3</sub>Au holograms without matrix effects. The experimental holograms in (a) are taken from Dul et al. (2013) and were measured by Karol Dąbrowski.

projection of the (111) plane. The profiles were fitted with

$$\chi_{\mathbf{H}}^{+}(\Delta\alpha) = \frac{A[|\mathbf{H}|^{2} + 2|\mathbf{H}|k\cos(\Delta\alpha + \delta)]}{[|\mathbf{H}|^{2} + 2|\mathbf{H}|k\cos(\Delta\alpha + \delta)]^{2} + (2k\Gamma)^{2}} + \frac{A[|\mathbf{H}|^{2} + 2|\mathbf{H}|k\cos(\Delta\alpha + \delta + \pi)]}{[|\mathbf{H}|^{2} + 2|\mathbf{H}|k\cos(\Delta\alpha + \delta + \pi)]^{2} + (2k\Gamma)^{2}},$$
(3.45)

where  $A = (-8\pi r_e/V) \operatorname{Re}(F_{i\mathbf{H}})$  and  $\delta$  is responsible for the position of the profile along  $\Delta \alpha$ . The fits are also presented in figure 3.7. All the theoretical curves resemble the experimental data. The most important fitted parameters are summarized in Table 3.1. From the fits it is also possible to determine the lattice constant a and the real part of the structure factors  $\operatorname{Re}(F_{i\mathbf{H}})$ . A and  $|\mathbf{H}|$ have been recalculated to  $\operatorname{Re}(F_{i\mathbf{H}})$  and a, respectively. The  $\Gamma$  parameter has an average value of  $\Gamma = 0.02 \text{ Å}^{-1}$  and this average value was used for the simulation of holograms in figure 3.6(c) and 3.6(d). Within the parameter uncertainties the fitted values of the lattice constant agree with the theoretical value of  $a = 3.753 \pm 0.005 \text{ Å}$ . The theoretical value of  $\operatorname{Re}(F_{i\mathbf{H}})$  for the consider  $\mathbf{H}$  vector should be equal to  $\operatorname{Re}(F_{i\mathbf{H}}) = 131.9$  for both  $i = \operatorname{Au}$  and  $i = \operatorname{Cu}$ . This value can be calculated with equation (1.15). The values of  $\operatorname{Re}(F_{i\mathbf{H}})$  obtained from the fits to the profiles from  $\chi_{\operatorname{Au}}^{\exp}$  and  $\chi_{\operatorname{Cu}}^{\exp}$ [figures 3.7(a) and 3.7(b)] strongly disagree with the expected theoretical value. After the correction for matrix effects the fits [figures 3.7(c) and 3.7(d)] yield  $\operatorname{Re}(F_{i\mathbf{H}})$  values which are in agreement with the theoretical value (within the fit uncertainties).

Table 3.1: Parameters fitted to the  $p_{(111)}$  profiles in figure 3.7.

	$\operatorname{Re}(F_{i\mathbf{H}})$	a [Å]	$\Gamma [\text{\AA}^{-1}]$
$\chi_{\rm Au}^{\rm exp}$	$69.8\pm 6.0$	$3.750 \pm 0.018$	$0.0212 \pm 0.0034$
$\chi^{ m exp}_{ m Cu}$	$56.4\pm6.4$	$3.749\pm0.024$	$0.0199 \pm 0.0043$
$\chi_{ m Au}$	$138 \pm 13$	$3.747\pm0.022$	$0.0207 \pm 0.0037$
$\chi_{ m Cu}$	$126\pm14$	$3.744\pm0.028$	$0.0193 \pm 0.0043$

Despite the slight differences between the amplitudes of the experimental and simulated holograms in figure 3.6 they are in good agreement between one another. All the main features of the experimental holograms can be identified in the simulated holograms. It needs to be said, however, that the differences between the gold and copper holograms are very small and can be noticed only after a detailed analysis of the holograms. The main difference can be seen in the hologram region which is marked by a white rectangle in figure 3.6. If we compare the holograms before and after the correction for matrix effects then the main difference between them is in the amplitude. For the non corrected holograms it is significantly lower then for the corrected ones. Apart from the amplitude, the gold and copper holograms recorded for  $Cu_3Au$  are quite similar and it is much easier to base the quantitative analysis of matrix effects on the structural images reconstructed from the holograms.



Figure 3.7: Fits (red solid lines) to the  $p_{(111)}$  profiles. (a) and (b) present fits to the  $p_{(111)}$  profiles from the  $\chi_{Au}^{exp}$  and  $\chi_{Cu}^{exp}$  holograms from figure 3.6(a). (c) and (d) present fits to the  $p_{(111)}$  profiles from the  $\chi_{Au}$  and  $\chi_{Cu}$  holograms from figure 3.6(b). The data are represented with blue dots which are connected with blue lines to guide the eye.

## STRUCTURE RECONSTRUCTION - THE PROBLEM OF THE COPPER ATOMS

To reconstruct the structure from the holograms in figures 3.6(a) and 3.6(b) we adopted the linear regression scheme proposed by Chukhovskii & Poliakov (2003) and described in Section 1.5. Since we have only one hologram, either Au or Cu, at our disposal the application of the holographic reconstruction scheme (Barton 1988, 1991) is impractical. For a reconstruction from just one hologram twin images persist and introduce a number of artifacts in the reconstruction image, hindering any quantitative analysis. Of course, by using the linear regression scheme we give up local structure analysis and focus on long range order.

In the linear regression scheme we take advantage of the centrosymmetricity of Cu<sub>3</sub>Au for which  $Im(F_{\rm H}) = 0$  and rewrite equation (1.16) as

$$\chi_i(\mathbf{k}) = \sum_{\langle hkl \rangle} \left( \operatorname{Re}\left[F_{ihkl}\right] \sum_{\mathbf{H}} \chi_{\mathbf{H}}^+ f(\mathbf{H}, hkl) \right)$$
(3.46)

where

$$f(\mathbf{H}, hkl) = \begin{cases} 1 & \text{if } |\mathbf{H}| = (2\pi/a)\sqrt{h^2 + k^2 + l^2} \\ 0 & \text{otherwise.} \end{cases}$$
(3.47)

In equation (3.46) it is assumed that the structure factors that correspond to crystallographically equivalent directions  $\langle hkl \rangle$  are equal, e.g.,  $\operatorname{Re}(F_{i001}) = \operatorname{Re}(F_{i010}) = \ldots = \operatorname{Re}(F_{i00\overline{1}})$ . Here, for convenience, we have changed the notation from  $F_{i\mathbf{H}}$  to  $F_{ihkl}$ .

With such a redefinition of equation (1.16) we can use the generalized least squares to fit  $\operatorname{Re}(F_{ihkl})$  with

$$\chi_{hkl}^{s} = \sum_{\mathbf{H}} \chi_{\mathbf{H}}^{+}(\mathbf{k}) f(\mathbf{H}, hkl)$$
(3.48)

as the basis functions. In figure 3.8(a) we can see an example of the  $\chi_{111}^s$  function. In figure 3.8(b) a single  $\chi_{\mathbf{H}}^+$  function for **H** that corresponds to [111] is shown.  $\chi_{111}^s$  is composed from four bands and four times more data will contribute to its fitting that to a single  $\chi_{\mathbf{H}}^+$  band.



Figure 3.8: A comparison of the  $\chi_{111}^s$  function (a) with the  $\chi_{\mathbf{H}}^+$  function (b) for  $\mathbf{H} = (2\pi/a)(1, 1, 1)$ . The calculation was performed for  $\Gamma = 0.02 \text{ Å}^{-1}$  and  $k = 8.8 \text{ Å}^{-1}$ .

The fitting of equation (3.46) to the holographic data was performed by solving  $(\mathbf{W}^{\mathrm{T}}\mathbf{W})\mathbf{F} = \mathbf{W}^{\mathrm{T}}\mathbf{b}$  [equation (1.31)] for **F**. The **W** matrix was filled with  $\chi_{hkl}^{s}(\mathbf{k})$  in the same way as it was filled with  $\chi_{\mathbf{H}}^{+}(\mathbf{k})$  in Section 1.5. Similarly, the **F** vector contained the real parts Re[ $F_{ihkl}$ ] of the structure factors and **b** was filled with the holographic data. Twenty-two basis functions  $\chi_{hkl}^{s}$ , up to  $|\mathbf{H}| = 5 \times (2\pi/a)$ , were used. The fits to the holograms are presented in figure 3.9. Apart from the fits the figure also presents the fitted real parts of the structure factors. The fitted structure factors were then used to reconstruct the electron density  $\rho_i$ . The reconstruction in the (001) plane is shown in figure 3.10. We will denote the reconstruction from  $\chi_{Au}^{exp}$  as  $\rho_{Au}^{exp}$  [figure 3.10(b)], from  $\chi_{Au}$  as  $\rho_{Au}$  [figure 3.10(c)] and from  $\chi_{Cu}$  as  $\rho_{Cu}$  [figure 3.10(d)].



Figure 3.9: Fits to the Cu<sub>3</sub>Au data from figures 3.6(a) and 3.6(b). Each row presents a fit to a different hologram. The left column presents the fitted real parts of the structure factors  $\text{Re}(F_{ihkl})$ . The right column presents the actual fits, where each plot was calculated with equation (3.46) by summing  $\text{Re}[F_{ihkl}]\chi^s_{hkl}$ .



before the matrix effects correction

Figure 3.10: Reconstruction of the Cu<sub>3</sub>Au holograms in the (001) plane (Dul et al. 2013). (a) and (b) are reconstructions before the correction for matrix effects from gold and copper holograms, respectively. (c) and (d) are reconstructions after the correction for matrix effects from gold and copper holograms, respectively. (e) is the schematic structure that is expected from the gold hologram whereas (f) is the schematic structure that is expected from the copper hologram. The white circles in the four reconstructions (a-d) mark the maxima which can be interpreted as copper atoms. Note, that the copper maxima have different amplitudes in (a) and (b), i.e., before the correction for matrix effects, the copper maxima have approximately the same amplitudes.

The electron density that one expects to obtain from a gold hologram, in the case of an ideal  $Cu_3Au$  crystal, is schematically shown in figure 3.10(e). Figure 3.10(f) shows the expected electron density that one expects to obtain from a copper hologram for an ideal  $Cu_3Au$  crystal. Figures 3.10(e) and 3.10(f) follow from our discussion at the beginning of Section 3.4.

If we compare the reconstructed electron densities in figures 3.10(a) and 3.10(b) with the expected ones then at first sight everything seems to be in order. The structures in the reconstruction resembles the expected ones. The most intense maxima in  $\rho_{Au}^{exp}$  can be attributed to gold atoms and the weakest maxima can be attributed to copper atoms. Similarly for  $\rho_{Cu}^{exp}$ , the most intense maxima can be attributed to the averaged electron density Au/3 + 2Cu/3 and the weakest maxima to copper atoms. However, the photon counts from which the  $\chi_{Au}^{exp}$  and  $\chi_{Cu}^{exp}$  holograms were obtained were measured at the same time during the same experiment. We would expect the maxima that we attribute to copper atoms in  $\rho_{Au}^{exp}$  and  $\rho_{Cu}^{exp}$  to have the same intensities. This is because the fluorescence from gold and copper was measured at the same time with an energy resolving detector. This is not the case. The maxima which we identified as copper atoms in  $\rho_{Au}^{exp}$  and  $\rho_{Cu}^{exp}$  have different intensities and the difference cannot be neglected. It is approximately ~ 37\%.

In the electron densities that we reconstructed from the holograms that were corrected for matrix effects the situation is different. Here as before, the reconstructed structures [figures 3.10(c) and 3.10(d)] resemble the expected ones. The most intense maxima in  $\rho_{Au}$  can be attributed to gold atoms and the weaker maxima can be attributed to copper atoms. As for  $\rho_{Cu}$  the most intense maxima can be attributed to the averaged electron density Au/3 + 2Cu/3 and the weaker ones to copper atoms. However, this time the maxima that we attribute to the copper atoms in  $\rho_{Au}$  and  $\rho_{Cu}$  have the same intensities (up to ~ 6%).

Note, that for  $Cu_3Au$ , matrix effects have only influenced the intensity of the maxima in the structure reconstruction. No, additional, spurious maxima can be observed. The reason for this lies in the structure of  $Cu_3Au$ . The structure around gold and copper atoms is the same. The differences lie only in site occupancy as argued in the Section 3.4. In the next Chapter we will consider the example of InAs where we will be confronted with the problem of spurious maxima in the reconstruction.

#### 3.8 Conclusions

In this Chapter we have considered matrix effects in XFH. We have:

- constructed a model which takes matrix effects into account in monochromatic XFH;
- shown that matrix effects may lead to a reduction of element sensitivity of the measured holograms;

- established that matrix effects may lead to distortions and/or spurious maxima in the reconstruction of atomic structure and that these distortions may hinder proper atomic structure analysis with XFH;
- proposed a correction procedure for matrix effects in monochromatic XFH; and
- validated our model on experimental data.

In the development of the model for matrix effects we have assumed that an energy resolving detector is used for the measurement of x-ray fluorescence. Such a setup is typical for x-ray fluorescence spectroscopy and significantly simplified the detection geometry and the calculations. In many XFH experiments, to achieve high count rates, researchers utilize avalanche photodiodes. Avalanche photodiodes have limited energy resolution and analyzing crystals are used to select the relevant characteristic fluorescence line (Tegze et al. 1999, Hayashi et al. 2001). We would like to point out that the proposed model can be easily extended to such and other detection geometries. This requires an integration of the outgoing fluorescence over the area from which fluorescence is collected.

As a final remark of this chapter we would like to discuss some of the limitations of the proposed model for matrix effects in XFH. An important situation in which the proposed model is not strictly valid is the Bragg condition. When the Bragg condition is fulfilled the absorption of a crystal, in particular a perfect crystal, dramatically decreases. This is known as the Borrmann effect (Borrmann 1950). The absorption is then not given by the standard absorption coefficients that we have used here. Moreover, at the Bragg condition so called extinction effects may become important. In particular, in imperfect crystals with a mosaic structure extinction effects can influence both the x-ray holograms as well as the reconstruction of atomic structure (Korecki, Novikov, Tolkiehn & Materlik 2004). Another situation in which our model must be used with care is the case of grazing angles, i.e., when  $\theta$  is close to 90°. In the experimental data that we have used the energy of the incident beam was set relatively high (E = 17.44 keV) and this minimized the extinction effects. The holograms were also measured only up to  $\theta = 80^{\circ}$  to avoid any grazing angle issues.

#### CHAPTER 4

# MATRIX EFFECTS IN WHITE BEAM XFH

In this chapter we extend the matrix effects model, developed in the previous chapter, to white beam XFH. In white beam XFH matrix effects are even more important than in monochromatic XFH. Due to the broadband nature of white x-ray spectra it is in many cases very difficult to avoid indirect excitation. This significantly limits the number of samples that can be studied with white beam XFH. In the presence of matrix effects, following the main results and conclusions of the previous chapter, we expect a reduction of element sensitivity of white beam holograms and an impact on structure reconstruction. The chapter is based on the work by Dul & Korecki (2015a).

#### 4.1 EXTENDING THE MODEL

We start the discussion of matrix effects in white beam XFH from equation (3.24). If a white beam is used in experiments then this equation needs to be integrated with respect to energy

$$\bar{Y}_{i,\lambda}(\theta,\phi) = \int_0^\infty Y_{i,\lambda}^0(E,\theta) \left[ 1 + \sum_n c_{i,n,\lambda}(E,\theta)\chi_n(E,\theta,\phi) \right] \mathrm{d}E.$$
(4.1)

In this section we explicitly write the dependence of  $\theta$ ,  $\phi$  and E in the equations. The incident energy spectrum  $I_0$  (now in units of photons/s/keV) is present in  $Y_{i,\lambda}^0$ . Equation (4.1) can be rewritten in a compact form as

$$\bar{Y}_{i,\lambda}(\theta,\phi) = \bar{Y}_{i,\lambda}^{0}(\theta) \left[ 1 + \sum_{n} \bar{\chi}_{i,n,\lambda}(\theta,\phi) \right], \qquad (4.2)$$

where

$$\bar{Y}^{0}_{i,\lambda}(\theta) = \int_{0}^{\infty} Y^{0}_{i,\lambda}(E,\theta) \mathrm{d}E$$
(4.3)

and the white beam hologram reads

$$\bar{\chi}_{i,n,\lambda}(\theta,\phi) = \frac{1}{\bar{Y}_{i,\lambda}^{0}(\theta)} \int_{0}^{\infty} Y_{i,\lambda}^{0}(E,\theta) c_{i,n,\lambda}(E,\theta) \chi_{n}(E,\theta,\phi) \mathrm{d}E.$$
(4.4)

At this point it is worthy to compare equation (4.2) with equation (2.1) which also gives the number of fluorescence photons measured by the detector, but for thin samples. In both equations we can distinguish the slowly varying term  $\bar{Y}^0_{i,\lambda}$  and a holographic part. In equation (2.1) the holographic

part consist of a single hologram  $\bar{\chi}_i$ , whereas in (4.2) it is given by a sum over the  $\bar{\chi}_{i,n,\lambda}$  holograms. Here we see the main difference between the thin and the thick sample case. For thin samples  $\bar{Y}_{i,\lambda}$  depends only on the hologram of the *i*th element. For thick samples it depends on holograms of all the elements in the sample because the  $\bar{\chi}_{i,n,\lambda}$  holograms contain the  $c_{i,n,\lambda}$  coefficients. For thin samples  $c_{i,n,\lambda} = \delta_{i,n}$  and equation (4.2) reduces to (2.1).

Equation (4.2) is a theoretical expression which binds the number of measured fluorescence photons and the holographic oscillations when the sample is thick. In the white beam case the holographic oscillation is retrieved from the measured fluorescence yield via

$$\bar{Y}_{i,\lambda}^{\exp}(\theta,\phi) = \bar{Y}_{i,\lambda}^{0,\exp}(\theta) \left[ 1 + \chi_{i,\lambda}^{\exp}(\theta,\phi) \right].$$
(4.5)

If we compare the right hand sides of equations (4.5) and (4.2) we obtain (Dul & Korecki 2015a)

$$\bar{\chi}_{i,\lambda}^{\exp}(\theta,\phi) = \sum_{n} \bar{\chi}_{i,n,\lambda}(\theta,\phi).$$
(4.6)

According to equation (4.6), the experimentally measured hologram cannot be regarded as element sensitive. In an ideal situation one would expect that  $\bar{\chi}_{i,\lambda}^{\exp}$  would contain only information about the structure around the *i*th element. Yet, due to the sum on the right hand side, it contains information about the structure around all elements in the sample. In this sense element sensitivity of  $\bar{\chi}_{i,\lambda}^{\exp}$  is reduced. This is an analogous result to (3.31) for monochromatic radiation. Note, that for thin samples  $\bar{\chi}_{i,\lambda}^{\exp} = \bar{\chi}_i$ .

The aim now, is to restore the element sensitivity of  $\bar{\chi}_{i,\lambda}^{\exp}$ . In a general case this seems to be hardly possible. To better highlight the problem let us consider a practical example of InAs (zincblende structure, space group  $F\bar{4}3m$ , lattice constant a = 6.058 Å). Please note, that in InAs arsenic atoms can be excited by indium K lines, since these lie above the arsenic K edge. For InAs equation (4.6) can be written as

$$\bar{\chi}_{\mathrm{In},\mathrm{K}\alpha}^{\mathrm{exp}}(\theta,\phi) = \bar{\chi}_{\mathrm{In},\mathrm{In},\mathrm{K}\alpha}(\theta,\phi) + \bar{\chi}_{\mathrm{In},\mathrm{As},\mathrm{K}\alpha}(\theta,\phi), \qquad (4.7a)$$

$$\bar{\chi}_{As,K\alpha}^{exp}(\theta,\phi) = \bar{\chi}_{As,In,K\alpha}(\theta,\phi) + \bar{\chi}_{As,As,K\alpha}(\theta,\phi).$$
(4.7b)

The left hand side in equations (4.7a) and (4.7b) is assumed to be known from experiment, i.e., it is assumed that two holograms are measured, one for In and one for As, each with K $\alpha$  radiation. The right hand side contains four pure terms ( $\bar{\chi}_{In,In,K\alpha}$ ,  $\bar{\chi}_{In,As,K\alpha}$ ,  $\bar{\chi}_{As,In,K\alpha}$ ,  $\bar{\chi}_{As,As,K\alpha}$ ) that need to be determined. Clearly, this is not possible since there are four unknowns and two equations. Adding additional equations for different energy lines or  $\theta_0$  angels does not help since each new equation adds two additional unknowns. In As is a simple case of a compound with just two elements. For compounds that contain more elements the number of unknowns is even greater.

Equations (4.7a) and (4.7b), or more precisely equation (4.6), might seem to be a dead end. Clearly, the system that results from (4.6) is underdetermined and at first sight nothing can be done

to solve it. However, if one takes a closer look at the  $c_{i,n,\lambda}$  coefficients one can observe that they have an asymptotic behavior for high energies. This fact can be used to push matters forward and obtain at least an approximate solution. To do so we examine how  $c_{i,n,\lambda}$  and  $Y_{i,\lambda}^0$  depend on energy.

# 4.2 The high energy limit

We first consider the energy dependence of the  $c_{i,n,\lambda}$  coefficients. Figure 4.1(a) presents the  $c_{i,n,\lambda}$  coefficients as a function of energy for our InAs example. The plots start just after the indium K edge. For all plotted coefficients an asymptotic behavior can be observed for energies far away from the indium K edge. The values of these asymptotes can be estimated in the following way. The  $c_{i,n,\lambda}$  coefficients depend on energy in a complicated way through  $\tau_{i,\lambda}^0(E)$ ,  $\tau_{j,\nu}^0(E)$ ,  $\mu(E)$  and  $\mu_n(E)$ . The dependence of the x-ray fluorescence cross section/mass attenuation coefficients on energy is complicated in general. Between the energy edges they can be, however, well approximated with the Victoreen (1943, 1948, 1949) equations:

$$\tau_{i,\lambda}^{0}(E) = \frac{a_{i,\lambda}}{E^{3}} + \frac{b_{i,\lambda}}{E^{4}},$$
(4.8a)

$$\tau_{j,\nu}^{0}(E) = \frac{a_{j,\nu}}{E^3} + \frac{b_{j,\nu}}{E^4},$$
(4.8b)

$$\mu(E) = \frac{a}{E^3} + \frac{b}{E^4} + d,$$
(4.8c)

$$\mu_n^0(E) = \frac{a_n}{E^3} + \frac{b_n}{E^4} + d_n, \tag{4.8d}$$

where  $a_{i,\lambda}$ ,  $b_{i,\lambda}$ ,  $a_{j,\nu}$ ,  $b_{j,\nu}$ , a, b,  $a_n$ ,  $b_n$ , d and  $d_n$  are constants. In (4.8a) and (4.8b) the free terms d and  $d_n$  are absent because  $\tau^0_{i,\lambda}$  and  $\tau^0_{j,\nu}$  are proportional only to the partial photoionisation cross sections. If we now substitute equations (4.8a), (4.8b), (4.8c) and (4.8d) into the expression for  $c_{i,n,\lambda}$  [equation (3.26)] and take the limit  $E \to \infty$  we obtain (Dul & Korecki 2015*a*)

$$c_{i,n,\lambda}^{\infty}(\theta) = \lim_{E \to \infty} c_{i,n,\lambda}(E,\theta)$$
$$= \frac{1}{H_{i,\lambda}^{\infty}(\theta)} \left[ c_{i,n,\lambda}^{\mathrm{BA},\infty}(\theta) + c_{i,n,\lambda}^{\mathrm{IE},\infty}(\theta) \right].$$
(4.9)

The  $H_{i,\lambda}^{\infty}$ ,  $c_{i,n,\lambda}^{\text{BA},\infty}$  and  $c_{i,n,\lambda}^{\text{IE},\infty}$  terms are given by

$$c_{i,n,\lambda}^{\mathrm{BA},\infty}(\theta) = \delta_{i,n} - \frac{d_n W_n \cos \theta_0}{d \, \cos \theta_0 + \mu(E_{i,\lambda}) \cos \theta},\tag{4.10}$$

$$c_{i,n,\lambda}^{\mathrm{IE},\infty}(\theta) = \sum_{j,\nu} \frac{a_{j,\nu} W_j \tau_{i,\lambda}(E_{j,\nu})}{2a_{i,\lambda}} \left[ \frac{\cos\theta}{d} \ln(u(\theta)) + \frac{\cos\theta_0}{\mu(E_{i,\lambda})} \ln(w) \right] \left[ c_{j,n,\lambda}^{\mathrm{BA},\infty}(\theta) + \mathfrak{d}\mathfrak{L}(\theta) \right], \quad (4.11)$$

$$\mathfrak{d}\mathfrak{L}(\theta) = -\frac{d_n W_n \left[ u(\theta) \,\mu(E_{j,\nu}) \cos\theta \ln(u(\theta)) - d \right]}{u(\theta) \, d^2 \,\mu(E_{j,\nu}) \left[ \cos\theta \ln(u(\theta))/d + \cos\theta_0 \ln(w)/\mu(E_{i,\lambda}) \right]},$$

and

$$H_{i,\lambda}^{\infty}(\theta) = 1 + \sum_{j,\nu} \frac{a_{j,\nu} W_j \tau_{i,\lambda}(E_{j,\nu})}{2a_{i,\lambda}} \left[ \frac{\cos\theta}{d} \ln(u(\theta)) + \frac{\cos\theta_0}{\mu(E_{i,\lambda})} \ln(w) \right]$$

with  $u(\theta) = 1 + d/ \left[ \mu(E_{j,\nu}) \cos \theta \right]$  and  $w = 1 + \mu(E_{i,\lambda}) / \left[ \mu(E_{j,\nu}) \cos \theta_0 \right]$ .

The values of the asymptotes in figure 4.1(a) can be now calculated with equation (4.9). The calculated values  $c_{i,n,\lambda}^{\infty}$  are marked with dashed horizontal lines. In the calculation we have used the *xraylib* library (Schoonjans et al. 2011) to obtain the necessary values of the x-ray fluorescence cross sections/mass attenuation coefficients. The necessary constants  $a_{i,\lambda}$ ,  $a_{j,\nu}$ , d and  $d_n$  have been obtained by fitting equations (4.8a), (4.8b), (4.8c) and (4.8d) to  $\tau_{i,\lambda}^0(E)$ ,  $\tau_{j,\nu}^0(E)$ ,  $\mu(E)$  and  $\mu_n^0(E)$ , respectively. The fits are presented in figure 4.2. As can be seen in figure 4.1(a), the agreement between the numerical asymptotes and the analytical estimates is good, although, for  $c_{As,As,K\alpha}$  and  $c_{As,In,K\alpha}$  the asymptotes are slightly shifted from the numerical values.



Figure 4.1: (a) The  $c_{i,n,\lambda}$  coefficients as a function of energy for InAs. The horizontal dashed lines mark the asymptotic behavior of the  $c_{i,n,\lambda}$  coefficients. (b) Energy dependence of  $Y_{i,n}^0$  and  $\sigma_i^0 I_0$ for indium and arsenic. All plots were calculated for  $\theta = 45^\circ$  and  $\theta_0 = 0^\circ$ . Figure taken from Dul & Korecki (2015*a*).

We now turn our attention to the energy dependence of  $Y_{i,\lambda}^0$ . Once again we first give an example for InAs which is presented in figure 4.1(b). In the figure both  $Y_{\text{In},K\alpha}^0$  and  $Y_{\text{As},K\alpha}^0$  have approximately the same shapes. This observation can be generalized for any two elements i, j and any two emission



Figure 4.2: Fits of equations (4.8a), (4.8b), (4.8c) and (4.8d) to  $\mu_{\text{In}}$ ,  $\mu_{\text{As}}$ ,  $\mu$  (for InAs),  $\tau^0_{\text{In},\text{K}\alpha}$ ,  $\tau^0_{\text{In},\text{K}\beta}$  and  $\tau^0_{\text{As},\text{K}\alpha}$ , respectively. XRF cross section stands for x-ray fluorescence cross section.

lines  $\lambda$ ,  $\nu$ . In the high energy limit we have (Dul & Korecki 2015a)

$$\lim_{E \to \infty} \frac{Y_{i,\lambda}^0(E,\theta)}{Y_{i,\nu}^0(E,\theta)} = y_{i,j,\lambda,\nu}(\theta), \tag{4.12}$$

where

$$y_{i,j,\lambda,\nu}(\theta) = \frac{g_{i,\lambda}W_i}{g_{j,\nu}W_j} \times \\ \times \frac{a_{i,\lambda}[d + \mu(E_{j,\nu})/\cos\theta_0]}{a_{j,\nu}[d + \mu(E_{i,\lambda})/\cos\theta_0]} \frac{H_{i,\lambda}^{\infty}(\theta)}{H_{i,\nu}^{\infty}(\theta)}.$$
(4.13)

To obtain equation (4.12) we have once again used the Victoreen equations (4.8a), (4.8b) and (4.8c) and substituted them into the expression for  $Y_{i,\lambda}^0$  and  $Y_{j,\nu}^0$ . According to equation (4.12)  $Y_{i,\lambda}^0$  and  $Y_{j,\nu}^0$  have the same shapes in the high energy limit, i.e., one can write  $Y_{i,\lambda}^0 = y_{i,j,\lambda,\nu}Y_{j,\nu}^0$ . As a side remark we recall that exactly the same procedure was used in Section 2.2 to show that the effective spectra  $N_i$  have nearly the same shapes. They are independent of the element from which

fluorescence is measured [c.f. equation (2.14)]. We will see later that  $Y_{i,\lambda}^0$  can be also treated as an effective spectrum for thick samples, but only in the high-energy limit.

#### 4.3 Correcting for matrix effects in white beam XFH

The limit  $E \to \infty$  must not be understood explicitly. We take this limit only to approximate the behavior of  $c_{i,n,\lambda}$  and  $Y_{i,\lambda}^0$  far from the K absorption edges. With the results from the previous Section, equation (4.6) can be rewritten as

$$\bar{\chi}_{i,\lambda}^{\exp}(\theta,\phi) = \sum_{n} c_{i,n,\lambda}^{\infty}(\theta) \bar{\chi}_{n}^{\infty}(\theta,\phi), \qquad (4.14)$$

where

$$\bar{\chi}_n^{\infty}(\theta,\phi) = \frac{1}{\bar{Y}^0(E,\theta)} \int_0^\infty Y^0(E,\theta) \chi_n(E,\theta,\phi) \mathrm{d}E.$$
(4.15)

To obtain equation (4.15) we have defined  $y_{j,\nu}/y_{i,\lambda} = y_{i,j,\lambda,\nu}$  and  $\bar{Y}^0 = \int_0^\infty Y^0 dE$ , where we have put  $Y^0 = y_{i,\lambda}Y_{i,\lambda}^0 = y_{j,\nu}Y_{j,\nu}^0$  since  $Y_{i,\lambda}^0$  and  $Y_{j,\nu}^0$  have approximately the same shapes as argued in Section 4.2. It must be noted that equation (4.14) holds only in the high energy range and only for appropriately shaped experimental spectra. By appropriately shaped energy spectra we mean those that have a lower cut off far above the K edges of the elements that constitute the sample. For InAs such example spectra are the Diamond I12 and the Petra III P61.1 in figure 2.1 (top row).

Equation (4.14) can be used as the basis for the correction for matrix effects in white beam XFH, in a similar manner as equation (3.31) was used to correct for matrix effects in monochromatic XFH. If we write equation (4.14) for our InAs example we obtain

$$\begin{bmatrix} \bar{\chi}_{\mathrm{In,K\alpha}}^{\mathrm{exp}}(\theta,\phi) \\ \bar{\chi}_{\mathrm{As,K\alpha}}^{\mathrm{exp}}(\theta,\phi) \end{bmatrix} = \underbrace{\begin{bmatrix} c_{\mathrm{In,In,K\alpha}}^{\infty}(\theta) & c_{\mathrm{In,As,K\alpha}}^{\infty}(\theta) \\ c_{\mathrm{As,In,K\alpha}}^{\infty}(\theta) & c_{\mathrm{As,As,K\alpha}}^{\infty}(\theta) \end{bmatrix}}_{\mathbf{C}^{\infty}} \begin{bmatrix} \bar{\chi}_{\mathrm{In}}^{\infty}(\theta,\phi) \\ \bar{\chi}_{\mathrm{As}}^{\infty}(\theta,\phi) \end{bmatrix}$$
(4.16)

which contains two unknowns  $\bar{\chi}_{\text{In}}^{\infty}$  and  $\bar{\chi}_{\text{As}}^{\infty}$ . With the help of the condition number it can be shown that equation (4.16) is a well-defined system of equations. Note, that in a general case, as for monochromatic radiation, the set of equations in (4.16) can be easily made overdetermined by measuring  $\bar{\chi}_{i,\lambda}^{\text{exp}}$  holograms for different elements, energy lines and  $\theta_0$  angles. In its structure (4.16) is analogous to equation (3.35).

# 4.4 Effect on local structure imaging

The proposed correction scheme for matrix effects in white beam XFH is based on the high energy limit. This limit is a rather crude approximation of realistic experimental conditions. In order to

show that the proposed correction procedure actually works for energy spectra generated by available bending magnets and wigglers we perform numerical model calculations for InAs. For this purpose we use the Diamond I12 spectrum from figure 2.1(top left corner) as  $I_0(E)$ . The spectrum has a lower cut off around ~ 40 keV which is ~ 12 keV above the In K edge. We first examine the effect of BA and IE on the holograms and then concentrate on their impact on local structure imaging.

As a first step we have calculated two holograms  $\bar{\chi}_{In}$  and  $\bar{\chi}_{As}$  without matrix effects. These holograms are needed for comparison purposes. They were calculated by a direct integration of equation (2.3) over energy. The single energy holograms  $\chi_i$  in (2.3) were calculated on a (361 × 600)  $(\theta \times \phi)$  grid for 40 Å clusters with equation (1.10). To mimic typical experiments conditions the  $\theta$ range was limited from 20° to 85° and  $\theta_0 = 0^\circ$ . Poisson-like noise which corresponded to 10<sup>7</sup> photons per pixel was added to the holograms. The calculated holograms  $\bar{\chi}_{In}$  and  $\bar{\chi}_{As}$  are shown in figures 4.3(a) and 4.3(b), respectively.

Next, we have calculated two holograms  $\bar{\chi}_{In,K\alpha}^{exp}$  and  $\bar{\chi}_{As,K\alpha}^{exp}$  with matrix effects. These holograms have been calculated explicitly with equations (4.7a) and (4.7a). All necessary parameters like the  $\theta$  range, cluster size etc. were the same as for  $\bar{\chi}_{In}$  and  $\bar{\chi}_{As}$ . The energy integral in equation (4.4) was evaluated numerically. Once the holograms with matrix effects were calculated they were corrected for the influence of matrix effects. The correction was made in accordance with equation (4.16). The equation was solved for every  $\theta$  angle by inverting the  $\mathbf{C}^{\infty}$  matrix. As a result two corrected holograms  $\bar{\chi}_{In}^{\infty}$  and  $\bar{\chi}_{As}^{\infty}$  were obtained. The calculated holograms  $\bar{\chi}_{In,K\alpha}^{exp}$  and  $\bar{\chi}_{As,K\alpha}^{exp}$  are shown in figures 4.3(c) and 4.3(d) whereas  $\bar{\chi}_{In}^{\infty}$  and  $\bar{\chi}_{As}^{\infty}$  are shown in figures 4.3(e) and 4.3(f), respectively. For comparison we also show crystal projections around In [figure 4.3(g)] and As [figure 4.3(h)] atoms.

The evaluation of the energy integrals in (2.3) and (4.4) requires some comment. The calculation of holograms through a direct integration over energy is a lengthy process. The energy integral has to be calculated for every  $(\theta, \phi)$  point in  $\chi_n$ . The holographic signal  $\chi_n$  is highly oscillatory and the integration step needs to be sufficiently small to achieve reasonable convergence. Moreover,  $\chi_n$  is given by a sum over atoms and has to be reevaluated for every energy step. This also extends the calculation time. Of course, for  $\bar{\chi}_{\text{In}}$  and  $\bar{\chi}_{\text{As}}$  we could have used equation (2.11) and approximate the effective spectrum with the Gumbel distribution. As shown in Section 2.2 this yields a nearly identical result as the direct numerical integration and the calculation lasts only a few minutes. However, to be consistent, we have decided to calculate all the holograms in the same way with a direct integration over the energy range. This process can be significantly sped up if one uses the symmetry of the InAs crystal. Then the monochromatic holograms can be generated in a very limited  $\theta - \phi$  range and the symmetry operations of the  $4\bar{3}m$  point group can be used to obtain the whole desired  $\theta - \phi$  range.

A comparison of the holograms without matrix effects [figures 4.3(a) and 4.3(b)] with the crystal structure projections [figures 4.3(g) and 4.3(h)] reveals the quasi-real space nature of white beam holograms. All the visible bands can be attributed to signals coming from crystallographic planes



without matrix effects

As holograms

In holograms

Figure 4.3: Simulated InAs holograms and crystal structure projections (Dul & Korecki 2015*a*). Holograms without matrix effects: (a)  $\bar{\chi}_{\text{In},K\alpha}$ , (b)  $\bar{\chi}_{\text{As}}$ ; with matrix effects: (c)  $\bar{\chi}_{\text{In},K\alpha}^{\exp}$ , (d)  $\bar{\chi}_{\text{As},K\alpha}^{\exp}$ ; corrected for matrix effects: (e)  $\bar{\chi}_{\text{In},K\alpha}^{\infty}$ , (f)  $\bar{\chi}_{\text{As}}^{\infty}$ . InAs atomic structure projections around In (g) and As (h) atoms. Atoms (balls) up to 5.05 Å from the central atom are marked in color and surrounded with circles. The size of atoms is inversely proportional to their distance from the central atom and proportional to their atomic number. The inner dashed circle marks  $\theta = 20^{\circ}$ , the outer dashed circle  $\theta = 85^{\circ}$  and the outer solid circle  $\theta = 90^{\circ}$ . Left halves of the holograms have no noise for better presentation. whereas the dark spots can be attributed to signals from atomic rows.

Let us first examine the effect of BA on white beam holograms. This can be done if we focus solely on the indium holograms. Indium atoms cannot be indirectly excited by arsenic atoms to emit K fluorescence. If we compare the pure indium hologram [figure 4.3(a)] with the one in which BA is present [figure 4.3(c)] then we can hardly notice any real differences. The only difference that can be seen is the slightly lower amplitude of  $\bar{\chi}_{\text{In},K\alpha}^{\exp}$  as compared to  $\bar{\chi}_{\text{In}}$ . The decrease of the amplitude is greater towards the edge of the hologram, i.e., towards  $\theta = 90^{\circ}$ . It can be concluded that the effect of BA on white beam holograms is very weak. This is in fact a quite general statement and follows from equation (3.27). If the x-ray energy spectrum has a lower cut off far above the K edge of the heaviest element in the sample then  $\mu(E_{i,\lambda}) \gg \mu_n^0(E)$  since  $E_{i,\lambda} \ll E$ . Because of this the  $\mu_n^0(E)W_n/\tilde{\mu}(E, \theta, E_{i,\lambda})\cos\theta$  term is strongly suppressed. The  $c_{i,n,\lambda}$  coefficients are then either close to one if i = n or close to zero if  $i \neq n$ . The hologram with BA is then nearly equal to the pure one  $\bar{\chi}_{i,\lambda}^{\exp} \approx \bar{\chi}_i$ . The small effect of BA have been observed (Korecki et al. 2011). As a final remark, we must note that towards grazing angles, when  $\theta$  is very close to 90°, the considered model is not fully applicable. In this region a more sophisticated approach is needed.

We now turn our attention to the arsenic holograms. Here the situation is completely different than for the indium ones. If we compare  $\bar{\chi}_{As,K\alpha}^{exp}$  with  $\bar{\chi}_{As}$  we can observe a number of differences. By means of the discussion in the previous paragraph we can conclude that these are mainly due to IE. The main difference between  $\bar{\chi}_{As,K\alpha}^{exp}$  and  $\bar{\chi}_{As}$  is in the intensity of the dark spots and the bands. In  $\bar{\chi}_{As}$  the bands, which correspond to signals from the {111} planes, are antisymmetric whereas in  $\bar{\chi}_{As,K\alpha}^{exp}$  they are symmetric. In  $\bar{\chi}_{As,K\alpha}^{exp}$  the dark spots, which correspond to the [111], [ $\bar{1}\bar{1}1$ ] and  $\langle 011 \rangle$ directions, are much darker than in  $\bar{\chi}_{As}$ . The overall amplitude of  $\bar{\chi}_{As,K\alpha}^{exp}$  is also reduced. Thus, IE significantly influences the  $\bar{\chi}_{As,K\alpha}^{exp}$  hologram. Most importantly, the expected shape of the arsenic hologram changes. All this might lead to distortions and/or spurious maxima in the reconstruction images. This was already suggested by Dabrowski et al. (2013), where white beam holograms for Cu<sub>3</sub>Au were measured in laboratory conditions. The results were, however, not conclusive due to the rather low quality of the data.

To show the effect of matrix effects on local structure imaging we apply the inverse windowed wavelet transform (c.f. Chapter 2) to the simulated holograms. However, before we do so we have to remark on the application of the IWWT to the InAs holograms with matrix effects and those corrected for matrix effects. For thick samples we can write equations (4.4) and (4.15) in a more general form as

$$\bar{\chi}(\theta,\phi) = \int_0^\infty N(E,\theta)\chi(E,\theta,\phi)\mathrm{d}E,\tag{4.17}$$

where  $N(E, \theta)$  denotes the generalized effective spectrum which can be equal to  $Y^0_{i,\lambda}(E, \theta)c_{i,n,\lambda}(E, \theta)$ 

or to  $Y^0(E, \theta)$ . The left hand side  $\bar{\chi}$  represents either  $\bar{\chi}_{i,n,\lambda}$  or  $\bar{\chi}_n^{\infty}$  and on the right hand side  $\chi$  represents  $\chi_n$ . Equation (4.17) can also represent equation (2.6) if we substitute  $\bar{\chi}_i$  for  $\bar{\chi}$ ,  $\chi_i$  for  $\chi$  and  $N_i(E)$  for  $N(E, \theta)$ . Equation (2.6) is the analog of (4.4) and (4.15), but for thin samples.



Figure 4.4: Comparison of various generalized effective spectra. (a) and (b) depict  $Y_{\text{As},K\alpha}^0$  and  $Y_{\text{In},K\alpha}^0$ , respectively. The spectra are plotted for different values of  $\theta$ . (c) and (d) depict comparisons of  $Y_{i,\lambda}^0$  and  $Y_{i,\lambda}^0 c_{i,n,\lambda}$ . In (d) the absolute value of  $Y_{\text{In},K\alpha}^0 c_{\text{In},\text{As},K\alpha}$  is plotted (the values of  $Y_{\text{In},K\alpha}^0 c_{\text{In},\text{As},K\alpha}$  are negative since  $c_{\text{In},\text{As},K\alpha} < 0$ ). All spectra are normalized to their maxima.

The whole formalism of wavelets is based on the assumption that the effective spectrum's shape does not depend on the relative sample-beam orientation. In equation (4.17) the generalized effective spectrum clearly depends on  $\theta$  which determines the sample-beam orientation. This, in principle, prohibits the usage of wavelets since the parameters  $k_0$  and  $\Delta k$  of the scaled mother wavelet (2.46) are determined from the shape of the effective spectrum. If the shape of the spectrum varies with  $\theta$  then the wavelet parameters must also vary with  $\theta$  and the wavelet loses its properties, most importantly the admissibility condition can be violated. Unfortunately, there is no easy exact solution to this problem. An approximate solution can be obtained if one notices that, although,  $N(E, \theta)$  depends
on  $\theta$ , this dependence is not strong and in many cases can be neglected. Herein, we have to remark that all the current approaches of structure retrieval for white beam holograms are based on the assumption that the effective spectrum does not change significantly with  $\theta$ .

The  $\theta$  dependence of the effective spectra was already noted for non-thin sample in the first white beam experiment (Korecki & Materlik 2001). There the authors have noted that although the shape of the spectrum depends on  $\theta$  it does not change much. It is only the amplitude that changes significantly. They have considered the  $\theta$  range from 0° to 55° which was the range in which the experiment was performed. In figures 4.4(a) and 4.4(b) we show  $Y_{i,\lambda}^0$  for indium and arsenic atoms and  $K\alpha$  lines for various values of  $\theta$ . The plots confirm the conclusions of Korecki & Materlik (2001). In a wide  $\theta$  range the shape of the spectra is nearly identical. It is only for  $\theta \gtrsim 80^{\circ}$  for which the peak of the spectrum starts to shift towards higher energies. For  $Y_{i,\lambda}^0 c_{i,n,\lambda}$  the  $c_{i,n,\lambda}$  coefficients do not introduce significant distortions to the shapes of the spectra since far from the absorption edges their values vary rather slowly with  $\theta$ . For comparison, two specific examples of  $Y_{i,\lambda}^0 c_{i,n,\lambda}$  are plotted in figures 4.4(c) and 4.4(d). Apart from  $Y_{\text{In},\text{K}\alpha}^0 c_{\text{In},\text{As},\text{K}\alpha}$  the shapes of the  $Y_{i,\lambda}^0 c_{i,n,\lambda}$  spectra are nearly the same as  $Y_{i,\lambda}^0$ . For  $Y_{\text{In},\text{K}\alpha}^0 c_{\text{In},\text{As},\text{K}\alpha}$  it is the position of the maximum which is shifted towards lower energies. For our particular example this does not introduce any obstacles since the value of  $c_{\text{In},\text{As},\text{K}\alpha}$  is close to zero [c.f. figure 4.1] and the contribution of  $\bar{\chi}_{\text{In},\text{As},\text{K}\alpha}$  to  $\bar{\chi}_{\text{In},\text{K}\alpha}^{\text{exp}}$  is negligible.  $\bar{\chi}_{\text{In,As,K}\alpha}$  should not contribute significantly to the IWWT image of  $\bar{\chi}_{\text{In,K}\alpha}^{\exp}$ . Thus, for the considered  $\theta$  range the effective spectra can be considered approximately constant in  $\theta$ . Moreover, the shape of  $Y_{i\lambda}^0$  is nearly identical to  $N_i = \sigma_i I_0$ . The comparison of the two is shown in figure 4.1(b).

The wavelet parameters  $k_0$  and  $\Delta k$  can be determined by fitting a Lorentzian (2.15) to  $\sigma_{\rm In}I_0$  and  $\sigma_{\rm As}I_0$ . The values that are obtained from the fits are  $k_0 = 36.2$  Å<sup>-1</sup> and  $\Delta k = 15.8$  Å<sup>-1</sup> for  $\sigma_{\rm In}I_0$  and  $k_0 = 36.5$  Å<sup>-1</sup> and  $\Delta k = 16.1$  Å<sup>-1</sup> for  $\sigma_{\rm As}I_0$ . With these values equation (2.61) can be used to apply the IWWT to the simulated InAs holograms. The obtained IWWT images are presented in figure 4.5. They have been calculated for a radial cut off distance  $r_c = 6$  Å and a lower radial cut off  $r_b = r_0 = 1$  Å. The images of  $\bar{\chi}_{\rm In}$ ,  $\bar{\chi}_{\rm In,K\alpha}^{\exp}$ ,  $\bar{\chi}_{\rm As}^{\infty}$ ,  $\bar{\chi}_{\rm As,K\alpha}^{\exp}$  and  $\bar{\chi}_{\rm As}^{\infty}$  are denoted with  $F_{\rm In}$ ,  $F_{\rm In,K\alpha}^{\exp}$ ,  $F_{\rm In}^{\infty}$ ,  $F_{\rm As}$ ,  $F_{\rm As,K\alpha}^{\exp}$  and  $F_{\rm As}^{\infty}$ , respectively.

In accordance with the results from Chapter 2 the IWWT images  $F_{\text{In}}$  and  $F_{\text{As}}$  [figures 4.5(a) and 4.5(b)] can be interpreted as projections of local atomic structure around In and As atoms, respectively. This is especially evident if one compares them with the crystal structure projections in figures 4.3(g) and 4.3(h). All the maxima in white circles in  $F_{\text{In}}$  and  $F_{\text{As}}$  can be attributed to signals from atoms which lie no further from the absorbing atom then 5.05 Å. The white circles correspond to the blacks ones in the crystal structure projections. All other maxima can be attributed to signals from atoms which lie further from the absorbing atom than 5.05 Å.

The  $F_{\text{In}}$ ,  $F_{\text{In},K\alpha}^{\exp}$  and  $F_{\text{In}}^{\infty}$  IWWT images [figures 4.5(a), 4.5(c) and 4.5(e)] do not show any significant differences. There are slight differences in the amplitudes but apart from that they are nearly identical. There are no artifacts or spurious maxima. The images qualitatively are in good



Figure 4.5: Inverse windowed wavelet transform (IWWT) images obtained from the (a)  $\chi_{In}$ , (b)  $\chi_{As}$ , (c)  $\chi_{In,K\alpha}^{exp}$ , (d)  $\chi_{As,K\alpha}^{exp}$ , (e)  $\chi_{In}^{\infty}$  and (f)  $\chi_{As}^{\infty}$  holograms. Atoms up to 5.05 Å from the absorber are marked with white circles. The inner dashed circle marks  $\theta = 20^{\circ}$ , the outer dashed circle marks  $\theta = 85^{\circ}$  and the solid outer circle marks  $\theta = 90^{\circ}$ .

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agreement because the indium holograms  $\bar{\chi}_{\text{In}}$ ,  $\bar{\chi}_{\text{In},K\alpha}^{\exp}$  and  $\bar{\chi}_{\text{In}}^{\infty}$  did not differ significantly. As already noted the impact of BA on white beam holograms is very weak. As a result its impact on structure reconstruction cannot be significant.

The situation is completely different for the  $F_{As}$ ,  $F_{As,K\alpha}^{exp}$  and  $F_{As}^{\infty}$  IWWT images [figures 4.5(b), 4.5(d) and 4.5(f)]. Here, if we compare  $F_{As}$  with  $F_{As,K\alpha}^{exp}$  we can observe a number of differences. Firstly, and most importantly, in  $F_{As,K\alpha}^{exp}$  we can observe two distinct maxima, marked with arrows, which are not visible in  $F_{As}$ . These can be attributed to signals originating from the nearest neighbors of indium atoms. The indium nearest neighbor atoms are also marked with arrows in figure 4.3(g). The positions of the nearest neighbor atoms and the additional maxima in  $F_{As,K\alpha}^{exp}$  coincide. Secondly, in  $F_{As,K\alpha}^{exp}$  the maxima in the  $\langle 011 \rangle$  directions are more intense than in  $F_{As}$ . Finally, signals which are closest to the outer dashed circle and the inner dashed circle in  $F_{As,K\alpha}^{exp}$  appear to be blurred. All these artifacts and spurious signals in  $F_{As,K\alpha}^{exp}$  appear because through  $\bar{\chi}_{As,In,K\alpha}$ ,  $\bar{\chi}_{As,K\alpha}^{exp}$  carries structure information about the surrounding of indium atoms. All the mentioned features could hinder proper local atomic structure imaging with white beam XFH. They could be, for example, misinterpreted as signals from atoms. Correcting for them is a necessity.

The IWWT image  $F_{\text{As},K\alpha}^{\infty}$  for the corrected arsenic hologram is free from the mentioned features. It is nearly identical to  $F_{\text{As}}$  although there is a slight difference in the amplitude between the two. The slight difference in the amplitude is due to the already mentioned fact that the proposed correction procedure is only approximate for spectra generated by real bending magnets or wigglers.

#### 4.5 Conclusions

In this Chapter we have considered matrix effects in white beam XFH. We have:

- proposed a model for matrix effects in white beam XFH;
- found that the effect of beam attenuation is very weak for high energies whereas indirect excitation is important throughout the whole energy range;
- shown that, similarly as in the monochromatic case, matrix effects lead to a reduction of element sensitivity of white beam holograms;
- shown using numerical calculation that matrix effects can change the amplitude as well as the shape of the holographic signal;
- explicitly shown that matrix effects may lead to distortions and/or spurious maxima in the reconstruction; and
- proposed an approximate correction procedure for matrix effects in white beam XFH in the high energy range.

Our discussion was based on general considerations and, at the same time, it was supported by an InAs example.

The description of matrix effects and most importantly the possibility of correcting for them opens way for proper atomic structure studies with white beam XFH. Such studies are cumbersome or impossible at all in the presence of matrix effects and without a way to tackle them.

#### CHAPTER 5

## SUMMARY AND OUTLOOK

In this work we have considered certain aspects in the description of XFH experiments and structure retrieval from x-ray fluorescence holograms.

In the first part we have focused on white beam XFH. We have introduced the Gumbel approximation of effective x-ray spectra which nearly perfectly matches their shape. This allowed us to significantly improve the description of white beam holograms. With this improvement in place, we have concentrated on structure retrieval. We have provided a quantitative description for the wavelet analysis of white beam holograms by deriving formulas for the radial and angular resolution. Although the resolution formulas were derived for the Lorentizan approximation of the effective energy spectra, they are quite general and give good estimates for the achievable resolution. Most importantly, it was explicitly shown that the wavelet analysis is sensitive to local atomic arrangements around the absorbing atoms. This was demonstrated through an academic example of a point scatterer chain and a realistic example of GaN. Unfortunately, for large systems of atoms, due to the non-orthogonality of the white beam holographic signal, the three dimensional reconstruction of the atomic structure with wavelets contains a significant number of artifacts which hinder proper atomic structure analysis. This problem can be overcome with the application of the inverse windowed wavelet transform. Computing the inverse windowed wavelet transform from its definition suffers from very long computing times and is highly impractical. We were able to reduce this calculation to a single integral over the surface of a sphere. This integral can be calculated in a fast single step. The inverse windowed wavelet transform provides two dimensional, artifact free projections of the local atomic structure around the absorbing atoms. The price that one pays for the lack of artifacts is a limited radial resolution which is compensated by a good angular resolution. We have shown that the inverse windowed wavelet transform can be used to image local atomic arrangements of impurities in the crystal lattice.

We have proposed a wavelet supported reliability factor (R-factor) analysis of holographic data. The analysis enables full three dimensional location of impurities that occupy multiple sites in the crystal lattice. For this purpose the inverse windowed wavelet transform was used. The proposed R-factor approach is sensitive to displacements of impurities from the exact lattice sites. In the future, the proposed wavelet based R-factor analysis could be extended to take into account local structure deformations around the impurities.

In the second part of this work we have dealt with the problem of matrix effects in XFH. We have concentrated on beam attenuation and indirect excitation. We have developed a model that

#### 5. Summary and outlook

takes these effects into account and argued that in their presence element sensitivity of the measured holograms might be reduced or even lost. Despite the fact that a hologram is measured with characteristic fluorescence radiation, it cannot be treated solely as a hologram originating from the element from which fluorescence is measured. It should be rather regarded as a weighted sum of holograms originating from all elements that significantly contribute to the sample's absorption coefficient. Furthermore, it was shown that the loss of element sensitivity can lead to distortions and/or spurious signals in the reconstruction images. This, in turn, can make the atomic structure analysis ambiguous.

To tackle the problem of element sensitivity reduction a correction procedure for matrix effects was developed. The procedure requires knowledge about the stoichiometry of the sample. For monochromatic XFH there are no significant restrictions on the applicability of the proposed correction procedure, however, care must be taken at the Bragg condition and for grazing angles. For these two cases the formalism of x-ray fluorescence spectroscopy, on which we have based our considerations, is not entirely valid. For white beam XFH the correction procedure is only approximate and only applicable in the high energy range, i.e., for energy spectra that have a lower cut off far from the K edge of the heaviest element in the sample. Although the correction is approximate, it was shown using numerical calculation for InAs, that it gives very good results.

The considerations of matrix effects and, in particular, the ability to correct for them is of great importance to both monochromatic and polychromatic XFH. Without accounting for matrix effects the number of samples that can be studied with XFH is significantly limited. This concerns multiple-energy XFH and, especially, white beam XFH, where is it very difficult to avoid indirect excitation due to the broadband nature of polychromatic x-ray spectra. The presented approach for tackling matrix effects might be extended to so called extinction effects. These have been studied in XFH (Korecki, Novikov, Tolkiehn & Materlik 2004) and it was shown that they also influence the holograms and structure reconstruction. The presented results might be also valuable for other methods, e.g., neutron holography (Cser et al. 2002, 2006) or the kinematical x-ray standing wave technique (Tolkiehn et al. 2005).

## APPENDIX

# DERIVIATION OF THE $c_{i,n,\lambda}$ COEFFICENTS

In Sections 3.2 and 3.3 we have derived a relation [equation (3.31)] between holograms measured in experiments  $\chi_{i,\lambda}^{\exp}$  and those that contain pure element specific information  $\chi_i$ . According to this relation the two are connected by the  $c_{i,n,\lambda}$  coefficients which are given by

$$c_{i,n,\lambda} = \frac{1}{Y_{i,\lambda}^{0}} \left( \frac{\partial Y_{i,\lambda}}{\partial \chi_{n}} \Big|_{\chi=0} \right).$$
(A.1)

To obtain a compact expression for  $c_{i,n,\lambda}$  one needs to calculate the partial derivative  $\partial Y_{i,\lambda}/\partial \chi_n\Big|_{\chi=0}$  which can be written as

$$\frac{\partial Y_{i,\lambda}}{\partial \chi_n} \bigg|_{\chi=0} = \frac{\partial Y_{i,\lambda}^{0,\text{DE}}}{\partial \chi_n} \bigg|_{\chi=0} + \frac{\partial Y_{i,\lambda}^{0,\text{IE}}}{\partial \chi_n} \bigg|_{\chi=0}.$$
(A.2)

The first term in the above equation is the direct excitation term while the second is the indirect excitation term. They can be written explicitly as

$$\frac{\partial Y_{i,\lambda}^{0,\text{DE}}}{\partial \chi_n} \bigg|_{\chi=0} = \frac{g_{i\lambda}}{\cos\theta} I_0 W_i \frac{\partial}{\partial \chi_n} \left[ \tau_{i,\lambda}^0(E) \left(1+\chi_i\right) \frac{1}{\widetilde{\mu}(E,\theta,E_{i,\lambda})} \right] \bigg|_{\chi=0}$$
(A.3)

and

$$\frac{\partial Y_{i,\lambda}^{0,\mathrm{IE}}}{\partial \chi_n}\Big|_{\chi=0} = \frac{g_{i\lambda}}{\cos\theta} I_0 W_i \frac{\partial}{\partial \chi_n} \left[ \frac{1}{\widetilde{\mu}(E,\theta,E_{i,\lambda})} \sum_{j,\nu} W_j \tau_{i,\lambda}^0(E_{j,\nu}) \tau_{j,\nu}^0(E) \left(1+\chi_j\right) \mathcal{L}(E,E_{i,\lambda},E_{j,\nu}) \right] \Big|_{\chi=0}$$
(A.4)

Equations (A.3) and (A.4) are after the (3.19a), (3.19b) and (3.19c) substitutions. We separately calculate (A.3) and (A.4).

To calculate (A.3) we note that

$$\frac{\partial\mu(E)}{\partial\chi_n} = \frac{\partial}{\partial\chi_n} \left[ \sum_j W_j \mu_j^0(E) (1+\chi_j) \right] = \mu_n^0(E) W_n \tag{A.5}$$

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and first calculate

$$\frac{\partial}{\partial\chi_n} \left[ \frac{1}{\tilde{\mu}(E,\theta,E_{i,\lambda})} \right] = \frac{\partial}{\partial\chi_n} \left( \sec\theta \sum_j \mu_j^0(E)(1+\chi_j) + \mu(E_{i,\lambda}) \sec\theta_0 \right)^{-1}$$
$$= -\left( \sec\theta \sum_j \mu_j^0(E)(1+\chi_j) + \mu(E_{i,\lambda}) \sec\theta_0 \right)^{-2} \times \mu_n^0(E) W_n \sec\theta$$
$$= -\frac{\mu_n^0(E) W_n \sec\theta}{\tilde{\mu}(E,\theta,E_{i,\lambda})^2}, \tag{A.6}$$

and

$$\frac{\partial}{\partial\chi_n} \left[ \frac{\chi_i}{\widetilde{\mu}(E,\theta,E_{i,\lambda})} \right] = \frac{1}{\widetilde{\mu}(E,\theta,E_{i,\lambda})} \left( \frac{\partial\chi_i}{\partial\chi_n} \right) + \chi_i \left( \frac{\partial}{\partial\chi_n} \frac{1}{\widetilde{\mu}(E,\theta,E_{i,\lambda})} \right) \\
= \frac{\delta_{in}}{\widetilde{\mu}(E,\theta,E_{i,\lambda})} - \chi_i \frac{\mu_n^0(E)W_n \sec\theta}{\widetilde{\mu}(E,\theta,E_{i,\lambda})}.$$
(A.7)

In (A.7) we have used  $\partial \chi_i / \partial \chi_n = \delta_{in}$ . With these two derivatives we can rewrite  $\partial Y_{i,\lambda}^{0,\text{DE}} / \partial \chi_n|_{\chi=0}$  as

$$\frac{\partial Y_{i,\lambda}^{0,\mathrm{DE}}}{\partial \chi_n}\bigg|_{\chi=0} = \frac{g_{i\lambda}}{\cos\theta} I_0 W_i \frac{\tau_{i,\lambda}^0(E)}{\widetilde{\mu}(E,\theta,E_{i,\lambda})} \left[\delta_{in} - \frac{\mu_n^0(E)W_n \sec\theta}{\widetilde{\mu}(E,\theta,E_{i,\lambda})}\right]$$
(A.8)

or by introducing  $c^{\mathrm{BA}}_{i,n,\lambda}$  as

$$\frac{\partial Y_{i,\lambda}^{0,\text{DE}}}{\partial \chi_n} \bigg|_{\chi=0} = \frac{g_{i\lambda}}{\cos\theta} I_0 W_i \frac{\tau_{i,\lambda}^0(E)}{\widetilde{\mu}(E,\theta,E_{i,\lambda})} c_{i,n,\lambda}^{\text{BA}}.$$
(A.9)

To calculate the derivative in equation (A.4) we first write the relevant part of the equation

$$\frac{\partial}{\partial \chi_n} \left( \frac{(1+\chi_j)}{\widetilde{\mu}(E,\theta,E_{i,\lambda})} \mathcal{L}(E,E_{i,\lambda},E_{j,\nu}) \right) = \mathcal{L}(E,E_{i,\lambda},E_{j,\nu}) \frac{\partial}{\partial \chi_n} \frac{1}{\widetilde{\mu}(E,\theta,E_{i,\lambda})} \\
+ \frac{1}{\widetilde{\mu}(E,\theta,E_{i,\lambda})} \frac{\partial \mathcal{L}(E,E_{i,\lambda},E_{j,\nu})}{\partial \chi_n} + \frac{\mathcal{L}(E,E_{i,\lambda},E_{j,\nu})}{\widetilde{\mu}(E,\theta,E_{i,\lambda})} \frac{\partial \chi_j}{\partial \chi_n} + \chi_j \frac{\partial}{\partial \chi_n} \frac{\mathcal{L}(E,E_{i,\lambda},E_{j,\nu})}{\widetilde{\mu}(E,\theta,E_{i,\lambda})}. \quad (A.10)$$

In the end we will put  $\chi = 0$  so the final term in the above equation does not need to be explicitly calculated since it will cancel out anyway. All that needs to be calculated is  $L'_n(E, E_{j,\nu}) = \partial L(E, E_{i,\lambda}, E_{j,\nu})/\partial \chi_n$  which reads

$$\frac{\partial \mathcal{L}(E, E_{i,\lambda}, E_{j,\nu}, \theta)}{\partial \chi_n} = \frac{\partial}{\partial \chi_n} \left[ \frac{\cos \theta}{2\mu(E)} \ln \left( 1 + \frac{\mu(E)}{\mu(E_{j,\nu})\cos \theta} \right) \right] \\
= \frac{\mu_n^0 W_n \cos \theta}{2\mu(E)^2} \ln \left( 1 + \frac{\mu(E)}{\mu(E_{j,\nu})\cos \theta} \right) + \frac{\cos \theta}{\mu(E)} \frac{1}{\left( 1 + \frac{\mu(E)}{\mu(E_{j,\nu})\cos \theta} \right)} \frac{\mu_n^0 W_n}{\mu(E_{j,\nu})}, \tag{A.11}$$

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where if we put  $Q = 1 + \mu(E)/(\mu(E_{j,\nu})\cos\theta)$  we obtain equation (3.29). With the help of equations (A.6), (A.10) and (A.11) can rewrite equation (A.4) as

$$\frac{\partial Y_{i,\lambda}^{0,\text{IE}}}{\partial \chi_n}\bigg|_{\chi=0} = \frac{g_{i\lambda}}{\cos\theta} I_0 W_i \frac{1}{\widetilde{\mu}(E,\theta,E_{i,\lambda})} \sum_{j,\nu} W_j \tau_{i,\lambda}^0(E_{j,\nu}) \tau_{j,\nu}^0(E) \mathcal{L}(E,E_{i,\lambda},E_{j,\nu},\theta) \times$$
(A.12)

$$\times \left( \delta_{jn} - \frac{\mu_n^0(E)W_n \sec \theta}{\widetilde{\mu}(E, \theta, E_{i,\lambda})} + \frac{\mathcal{L}'_n(E, E_{j,\nu}, \theta)}{\mathcal{L}(E, E_{i,\lambda}, E_{j,\nu}, \theta)} \right)$$
(A.13)

or with the introduction of  $c^{\mathrm{IE}}_{i,n,\lambda}$  as

$$\frac{\partial Y_{i,\lambda}^{0,\mathrm{IE}}}{\partial \chi_n} \bigg|_{\chi=0} = \frac{g_{i\lambda}}{\cos\theta} I_0 W_i \frac{\tau_{i,\lambda}^0(E)}{\widetilde{\mu}(E,\theta,E_{i,\lambda})} c_{i,n,\lambda}^{\mathrm{IE}}.$$
(A.14)

We now add equations (A.9) and (A.14) and divide them by  $Y_{i,\lambda}^0$  [given by equation (3.17)] obtaining the final result

$$\frac{1}{Y_{i,\lambda}^{0}} \left( \frac{\partial Y_{i,\lambda}}{\partial \chi_{n}} \Big|_{\chi=0} \right) = \frac{1}{H_{i,\lambda}} \left( c_{i,n,\lambda}^{\mathrm{BA}} + c_{i,n,\lambda}^{\mathrm{IE}} \right) = c_{i,n,\lambda}.$$
(A.15)

## LIST OF SYMBOLS AND ABBREVIATIONS

Some symbols and abbreviations used throughout the text:

2D, 3D	Two and three dimensional.
BA	Beam attenuation.
$\operatorname{CSWT}$	Continuous spherical wavelet transform.
FWHM	Full width at half maximum.
IE	Indirect excitation.
IWWT	Inverse windowed wavelet transform.
XAFS	X-ray absorption fine structure.
XFH	X-ray fluorescence holography.
hkl	Integers. Throughout the text $k$ is also used to denote the
	magnitude of the wave vector. It should be clear from the
	context when $k$ is an integer and when it is not.
[hkl]	Indices of a crystal direction.
$\langle hkl  angle$	Indices of a set of all symmetrically equivalent crystal directions.
(hkl)	Indices of a lattice plane (Miller indices).
$\{hkl\}$	Indices of all symmetrically equivalent crystal planes
(h, k, l)	A vector with integer coefficients.

- $\chi_i$  Monochromatic x-ray fluorescence hologram from element *i*.
- $\bar{\chi}_i$  White beam x-ray fluorescence hologram from element *i*
- $\tilde{\chi}_i$  Continuous spherical wavelet transform of  $\bar{\chi}_i$ .
- $F_i$  Inverse windowed wavelet transform of  $\bar{\chi}_i$ .
- $\mathbf{k}$  Vector that is antiparallel to the wave vector  $\mathbf{k}_{\mathbf{x}}$  and has the same magnitude  $(\mathbf{k} = -\mathbf{k}_{\mathbf{x}})$ .
- **H** Reciprocal lattice vector.

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