Structure Modeling with X-ray Absorption and Reverse Monte Carlo: Applications to Water

Mikael Leetmaa
Abstract

Water is an important substance. It is part of us, of our environment, and is a fundamental prerequisite for the existence of life as we know it. The structure of water is still, after over 100 years of research on the subject, however under debate. In this thesis x-ray absorption spectroscopy (XAS) and reverse Monte Carlo (RMC) modeling are used to search for structural solutions of water consistent with many different experimental data sets, with emphasis on the combination of different experimental techniques for a reliable structure determination. Neutron and x-ray diffraction are analyzed in combination with the more recent synchrotron radiation based XAS. Geometrical criteria for H-bonding are implemented in RMC to drive the fits and allow to evaluate differently H-bonded structure models against the data. It is shown that the available diffraction data put little constraints on the type of H-bond topology or O-O-O tetrahedrality for the structure of liquid water. It is also demonstrated that classical MD simulations, using some of the most common interaction potentials for water, give rise to O-O and O-H pair-correlation functions with too sharp first peaks at too short distances to be in agreement with diffraction, and furthermore that requiring a large fraction of broken H-bonds is not in itself enough for a structure model to reproduce the experimental XAS. A contribution to the theoretical description of XAS is made by an in-depth investigation of important technical aspects of the TP-DFT spectrum calculations. A novel approach to RMC, applicable also to data that require a significant amount of computer time to evaluate, is developed which makes use of pre-computed properties from a large set of local geometries allowing RMC simulations directly on data from core-level spectroscopies such as XAS.

Avhandling som med tillstånd av Stockholms Universitet framlägges till offentlig granskning för avläggande av doktorsexamen i kemisk fysik.

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List of Papers

This thesis is based on the following six papers which will be referred to in the text by their Roman numbers, as Paper I, Paper II, etc. Reproduction of Papers I, II and III was made with kind permission from the publishers.

I. Are recent water models obtained by fitting diffraction data consistent with infrared/Raman and x-ray absorption spectra?, M. Leetmaa, M. Ljungberg, H. Ogasawara, M. Odelius, L-Å. Näslund, A. Nilsson and L.G.M. Pettersson  


IV. Theoretical Approximations to X-ray Absorption Spectroscopy of Liquid Water and Ice M. Leetmaa, M.P. Ljungberg, A. Lyubartsev, A. Nilsson and L.G.M. Pettersson  
*Submitted*

V. SpecSwap-RMC: A novel reverse Monte Carlo approach using a discrete set of local configurations and pre-computed properties M. Leetmaa, K.T. Wikfeldt and L.G.M. Pettersson  
*Submitted*

VI. Oxygen-oxygen correlations in liquid water; addressing the discrepancy between diffraction and EXAFS using a novel multiple-data set fitting technique K.T. Wikfeldt, M. Leetmaa, A. Mace, A. Nilsson and L.G.M. Pettersson  
*Submitted*

Related work to which I have contributed but not included in the thesis:

Comment on My Contributions

The research making up the content of this thesis (Papers I to VI) is the result of an extensive team-work, where many people have contributed with their special knowledge and abilities, all important for the final outcome of the papers. I was involved from an early stage in the manuscript preparation for all papers, except for Paper VI, where I took part in the writing at a later stage. I performed all StoBe spectrum calculations and related analyses in Papers I, II, IV and V. I performed all RMC simulations and diffraction analyses in Papers II and III in close collaboration with Thor Wikfeldt. I did all implementations in the RMC++ code, except for the implementation of the E-field representing IR/Raman which was mostly done by Mathias Ljungberg. I developed and implemented the SpecSwap-RMC method of Papers V and VI. All EXAFS and FEFFIT calculations, the implementation of the structure analysis package based on the SpecSwap weights used in Paper VI, as well as the SpecSwap-RMC simulations in paper VI were performed by Thor Wikfeldt. All work related to the IR/Raman spectroscopy, the GPAW calculations in Paper IV, as well as the theory section D in Paper IV concerning excited state DFT was done by Mathias Ljungberg.
“It might be well for all of us to remember that, while differing widely in the various little bits we know, in our infinite ignorance we are all equal.” [1]
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<tr>
<td>CEBE</td>
<td>core-electron binding energy</td>
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<tr>
<td>CPMD</td>
<td>Car-Parinello MD</td>
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<td>DFT</td>
<td>density functional theory</td>
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<tr>
<td>DD</td>
<td>double-donor</td>
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<tr>
<td>ΔKS</td>
<td>delta Kohn-Sham</td>
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<td>EXAFS</td>
<td>extended x-ray absorption fine structure</td>
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<tr>
<td>EPSR</td>
<td>empirical potential structure refinement</td>
</tr>
<tr>
<td>FCH</td>
<td>full core-hole</td>
</tr>
<tr>
<td>FNC</td>
<td>fixed neighbor constraints</td>
</tr>
<tr>
<td>FT</td>
<td>Fourier transform</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
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<tr>
<td>HCH</td>
<td>half core-hole</td>
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<tr>
<td>HSMC</td>
<td>hard sphere Monte Carlo</td>
</tr>
<tr>
<td>H-bond / HB</td>
<td>hydrogen-bond</td>
</tr>
<tr>
<td>MAFF</td>
<td>modified atomic form factors</td>
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<tr>
<td>MD</td>
<td>molecular dynamics</td>
</tr>
<tr>
<td>MMC</td>
<td>Metropolis Monte Carlo</td>
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<tr>
<td>ND</td>
<td>neutron diffraction</td>
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<tr>
<td>PCF</td>
<td>pair-correlation function</td>
</tr>
<tr>
<td>PIMD</td>
<td>path integral MD</td>
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<tr>
<td>PSF</td>
<td>partial structure factor</td>
</tr>
<tr>
<td>RMC</td>
<td>reverse Monte Carlo</td>
</tr>
<tr>
<td>SD</td>
<td>single-donor</td>
</tr>
<tr>
<td>SEY</td>
<td>secondary electron yield</td>
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<tr>
<td>TEY</td>
<td>total electron yield</td>
</tr>
<tr>
<td>TP</td>
<td>transition potential</td>
</tr>
<tr>
<td>XAS</td>
<td>x-ray absorption spectroscopy</td>
</tr>
<tr>
<td>XCH</td>
<td>excited core-hole</td>
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<tr>
<td>XD</td>
<td>x-ray diffraction</td>
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Chapter 1

Introduction

“The common assumption that water is well characterized has led to explanatory edifices built on shaky ground. The situation is unsatisfactory intellectually and hazardous in practice.” [2]

Water is an important substance. It is part of us, our environment, and a fundamental prerequisite for the existence of life as we know it. Water plays a central role in practically all human activity. It is one of the fundamental natural resources around which human society is built. Its importance can hardly be exaggerated [3]. Accordingly, water is one of the most studied compounds [4]. But there are still unresolved and disputed issues. The main focus of this thesis will be on the structure of liquid water at a molecular level, as determined from diffraction and spectroscopy.

The importance of water in society is intimately linked to the role of water in biology. Water is the biological solvent. The only one known that supports the existence of life. Water is not only a passive background, but an active participant in many molecular processes of biological relevance, such as transport phenomena and protein folding [5]. But does the structure of water really matter? If we by the structure of water mean a detailed description of the water-water interactions, and how, due to these interactions, the water molecules tend to arrange geometrically with respect to each other, then it certainly does. Not the least in molecular biology [2].

In 2004, a combined experimental and computational x-ray absorption spectroscopy (XAS) study on water [6] triggered a debate concerning the number of strong hydrogen bonds in liquid water. Based on a comparison between the experimental XAS spectra of liquid water, ice Ih and that of the ice surface, Wernet et al. proposed the number of hydrogen bonds in water to be close to two per molecule, with emphasis on an asymmetrically distorted local configuration. This is in sharp contrast to the commonly accepted picture of water, based largely on the analysis of diffraction data, as having close to four hydrogen bonds per molecule in a distorted ice-like tetrahedral network.

The proposed structure from Wernet et al. [6] can be considered the starting point for this thesis. We will in Papers I-VI examine the information content in available diffraction data, and test differently H-bonded structure models of water against XAS. Also the XAS calculations will be closely examined. A method for structure modeling of computationally demanding techniques is finally developed
and subsequently applied to study the structure of liquid water from EXAFS and diffraction. Chapters 2 and 3 of this thesis describe the main methods used, while the results from Papers I-VI are summarized in Chapter 4.

1.1 Background

Throughout this thesis we will be concerned with aspects of the structure of liquid water. We will therefore start by giving a brief introduction to liquid structure in general and the structure of liquid water in particular, as well as a short historical background to our work.

1.1.1 Pair-Correlation Functions

The structure of a disordered condensed material can be characterized in terms of its pair-correlation functions (PCFs). The PCF (often denoted \( g(r) \)) describes how the density varies around an atomic center, and is defined as the probability of finding an atom at a given distance from a central atom, averaged over all directions in space and normalized to the mean density of the material \( \rho_0 \). The local density \( \rho(r) \) at distance \( r \) from the atomic center, is thus given by \( \rho(r) = \rho_0 g(r) \) \([7]\), and the number of neighboring atoms \( n_{r_1,r_2} \) within an interval \( [r_1, r_2] \) can be obtained by integrating the PCF \([8]\) according to

\[
n_{r_1,r_2} = 4\pi \rho_0 \int_{r_1}^{r_2} r^2 g(r) dr
\]

(1.1)

In a close-packed liquid interacting via a simple pair-potential, such as the Lennard-Jones potential or a hard sphere repulsive potential (see e.g. ref. [9]), the PCF has a first sharp peak corresponding to the nearest neighbor distance. It then shows oscillatory behavior with broad bumps of decreasing height corresponding to 2\(^{nd}\) and 3\(^{rd}\) shell neighbors etc., until the local structural correlations die out and \( g(r) \) reaches its asymptotic value of 1. If there is more than one element present in the material there will be one PCF for each unique pair of atom types.

For a hydrogen-bonded (H-bonded) molecular liquid such as water the PCFs show a more complex behavior. The first-shell peak in the O-O PCF of liquid water is centered around 2.8 Å, much further out than what would be expected if water were a close-packed system, and the O-H and H-H correlations are complicated from the directionality of the H-bonds (Figure 4.9). Integrating the first peak in the O-O PCF for water as determined by x-ray diffraction gives a value of first-shell nearest neighbors around 4.5, and the local structural correlations die out at around 8 Å\([10, 11]\).

1.1.2 Early Diffraction Studies

X-ray diffraction (XD) from a disordered material gives information about the pair-correlations. In particular, for liquid water, the molecule-molecule PCF is obtained via a Fourier transform of the measured structure factor \( S(Q) \). Since the hydrogens scatter x-rays only weakly, to a first approximation the Fourier transform of the measured \( S(Q) \) can be considered to give information about the O-O PCF. Because
1.1. BACKGROUND

it is such a direct probe of the pair-correlations, analysis of diffraction data on water has played an essential role in establishing the presently dominating structure model of liquid water as a distorted ice-like tetrahedral network, with on the average slightly less than 4 H-bonds per water molecule.

The XD pattern of liquid water has been measured numerous times over the years. In 1933 Bernal and Fowler [12] analyzed the then available XD data, to conclude a quartz-like tetrahedral structure of the liquid at ambient conditions. Five years later Morgan and Warren presented XD measurements of liquid water at five different temperatures [10]. They considered their results to be in agreement with those of Bernal and Fowler, however they concluded a more ice-like structure for water [10]. The conclusion of an ice-like tetrahedral water structure was based on the first-shell coordination number of slightly more than 4 nearest neighbors, as well as the presence of the 2nd nearest neighbor distance at around 4.5 Å, and a comparison of the distance distribution of water, $4\pi\rho_0g(r)$, with a smoothed out ice-like distribution and found semi-qualitative agreement.

1.1.3 Structure Models

The role and meaning of a structure model has changed over time. Nowadays the concept of a structure model usually refers to a large set of atomic coordinates, placed in a box with periodic boundaries. However, such an explicit structure model of a disordered material only became possible with the introduction of computer simulations. There are other ways to think of a structure model.

In structure analysis of a crystalline material it is often sufficient to specify the type of lattice, the lattice parameters and the mean displacements from the perfect lattice positions. It is then understood that the unit cell of the structure is repeated infinitely in all directions. A similar type of structure models can be used for a disordered material, although in that case the unit cell is instead thought of as some local structural motif repeated imperfectly so that the structural correlations die out after a certain distance. To obtain the PCF from such a structure model is less straightforward and requires a detailed set of rules how the local structures should be repeated in space.

In a paper from 1969 Narten and Levy presented a number of conditions which must be met by any structure model to be tested against diffraction data [11]. The conditions were primarily aimed at producing structure models detailed enough on a molecular level so that the PCFs could be readily estimated. With todays computer-generated large periodic structure models the problem of testing against diffraction data is trivial. The PCFs can be directly calculated from the atomic positions. However, at the time this posed a real and important problem. A whole range of different structure models were examined but of the few detailed enough to be tested against diffraction data, only the ice-I model was considered in agreement with diffraction [11]. The ice-I model was similar to what Morgan and Warren had proposed for the structure; an open network structure closely related to a slightly expanded ice Ih, with spaces between the tetrahedrally bonded water molecules large enough to accommodate additional water molecules.

To account for the thermodynamical anomalies of water, two-state mixture model descriptions have over the years been quite popular, from the first postulation of different components in water to account for the density maximum in the 1890s
CHAPTER 1. INTRODUCTION

([13] and references therein), to later more sophisticated models [14]. In a mixture model the presence of two or more distinct species of water molecules is assumed, and the different species are usually associated with different local densities. Few if any of these thermodynamical models have been detailed enough on a molecular level to be tested against diffraction data. Narten and Levy concluded, based on small angle x-ray scattering (SAXS) [11], that density inhomogeneities in the liquid could not be as large as 20%. A statement which still leaves lots of room for speculations in terms of structure models. An interesting review of thermodynamical mixture models of water from the mid 1970s can be found in ref. [15].

1.1.4 MD Water and Diffraction

The idea behind molecular dynamics (MD) simulations is to start with a box of atoms, specify their positions and momenta as well as an interaction potential governing the forces between the atoms, and propagate the system in time by numerically solving the classical equations of motion for all atoms. A thermodynamical ensemble of choice is simulated (often an $\text{NVT}$ or $\text{NPT}$ ensemble) and ensemble averages are obtained as time averages [9]. By this means both thermodynamical and structural information can be obtained for a system, provided that the classical description of the dynamics is accurate enough and the interaction potential used realistically describes the system which it is supposed to model.

MD simulations made their first appearance in the field of water research in the late 1960’s, through the pioneering work of Barker and Watts [16] and that of Rahman and Stillinger [8], and gained increasing popularity along with the development of computer technology and efficient algorithms [9]. Today, MD simulations have taken a dominant position in the study of liquid water. All classical MD simulations of liquid water at ambient conditions with realistic potentials give rise to structures which are slight variations of the distorted ice-like tetrahedral network model. This model has become the textbook picture of liquid water structure.

When the popular SPC/E MD potential was constructed, it was noted that a potential employing a repulsive term proportional to $r^{-12}$ (as most simple potentials with a Lennard-Jones term do [9]) results in a first peak in the O-O PCF at a too short distance and too sharp and high compared to a PCF derived from x-ray diffraction data [17]. However, at the time, this was considered of minor importance. In later years there have appeared diffraction studies in the literature with PCFs similar to those from SPC/E [18, 19, 20]. In the neutron diffraction (ND) study of Soper and co-workers from 2000 [18] however, the MD like PCFs were the result of a too hard repulsive reference potential in combination with a lack of detailed information on intermolecular O-O correlations in the ND data [21]. In 2003 Head-Gordon and co-workers presented an x-ray diffraction study [20] with an O-O PCF in agreement with that from the neutron study of ref. [18]. However no fitting of the data was made in ref. [20] but instead the PCFs from the MD model which gave the best description of the data was taken as the benchmark PCFs. While claims were made that x-ray and neutron diffraction data finally agreed on the PCFs, the experimentally derived PCFs were highly biased towards results from MD simulations.

Soper published in 2007 a new diffraction study on water using the EPSR fitting technique, where a new set of PCFs were derived in a joint structure refinement
with both x-ray and neutron diffraction [21]. A much softer reference potential was
needed to fit the x-ray diffraction data at higher Q-values [21], and resulted in an
O-O PCF much resembling those from earlier x-ray diffraction studies [22]. These
latest results using the EPSR fitting technique are consistent with our reported PCFs
from RMC simulations of x-ray and neutron diffraction data in Papers II and III (see
Chapter 3 for a description of the EPSR and RMC methods), however with these
new studies, a majority of MD simulations of water can no longer be considered in
particularly good agreement with diffraction.

1.2 A Note on Structure Modeling

Throughout this theses the approach has been taken to include many different struc-
tural probes in the modeling of water, with the aim to obtain a consistent picture of
the structure. Different experimental probes are sensitive to different aspects of the
structure. Diffraction data on water, as discussed above, give important information
on pair-correlations. The full set of PCFs as determined from diffraction narrows
down the range of possible structure models substantially, but does not provide a
complete picture of the structure. Additional information has to be incorporated.
In this thesis we focus mainly on x-ray absorption spectroscopy (see Chapter 2) and
diffraction, and also to a lesser extent on vibrational spectroscopy (in Papers I and
II), and EXAFS (in Paper VI). The combination of different techniques is essential
for a correct structural determination.
Chapter 2

XAS Calculations

X-ray absorption spectroscopy (XAS)\(^1\) is a core-level spectroscopy. Core-level spectroscopies have their name from the involvement of core-level electrons in the spectroscopic process. In an independent-particle picture XAS can be thought of as an incoming x-ray photon being absorbed by a core-level electron, which gets excited. The process then has a certain probability depending on the properties of the initial and final state wave functions, their relative energies and the photon energy.

Within the important dipole approximation (Section 2.1.1 below) certain selection rules apply; total spin is conserved during excitation and the angular momentum \(l\) is changed by \(\pm 1\), thus for excitations from the 1s level only unoccupied states with local \(p\)-character are probed. Exciting from the oxygen \(K\)-edge therefore gives information about the unoccupied \(p\)-density of states in the presence of a core-hole. Due to the involvement of localized core-levels XAS becomes a local probe around specific atomic centra, however the spatial extent of the final states provides the spectroscopy with its structural sensitivity. The spectroscopic process is ultra fast (on an atto-second time scale), so that nuclear movement during the excitation can be completely neglected.

We will in this thesis mostly be concerned with the near-edge absorption of x-rays at the oxygen \(K\)-edge in water, spanning an energy range from the absorption onset at around 533 eV up to roughly 15 eV above the edge. Whenever the term XAS is used this is what we refer to. The near-edge spectrum can conveniently be described within a molecular orbital picture using the transition potential TP-DFT approach [23], which will be the subject of Section 2.3 below, after a brief introduction to density functional theory (DFT) in Section 2.2. Paper IV gives an extensive overview of the TP-DFT spectrum calculations on water in gas phase, liquid and ice. Results with more direct implications for the interpretation of XAS on water will be presented in Chapter 4 of this thesis while more technical aspects concerning augmentation basis set description, broadening and functional dependence will be discussed already in Section 2.3 below.

Higher up in energy, constructive and destructive interference of the ejected photo-electron scattered against the nearest atomic neighbors leads to a modulation of the absorption cross-section with energy referred to as EXAFS oscillations (for 1 Or NEXAFS for near-edge x-ray absorption fine structure, or XANES for x-ray absorption near edge structure.)
extended x-ray absorption fine structure). Although some EXAFS calculations and data appear in Papers V and VI it is not our main focus in this thesis, and no account for the theory of EXAFS will be given here. We refer instead to the work of Rehr and Albers [24] for a description of the multiple-scattering approach to x-ray absorption most conveniently used to describe EXAFS.

2.1 X-ray Absorption Spectroscopy (XAS)

Below is a short account of the theoretical description of XAS needed to appreciate the following discussion on spectrum calculations, however the theory described here is by no means unique for this thesis. For the discussion below leading up to Fermi’s “golden rule”, the books by Landau [25], Moss [26] and Townsend [27] were used as references. Especially useful as a reference on XAS in general is the book by Stöhr [28].

If at time \( t = 0 \) a system is in an initial state \( |i\rangle \), a standard time-dependent perturbation treatment [27] gives us the expansion coefficient \( c_{fi}(t) \) of the final state \( |f\rangle \) for \( f \neq i \) at time \( t \) to first order as

\[
c_{fi}(t) = -\frac{i}{\hbar} \int_0^t dt' e^{i\omega_{fi} t'} \langle f(0)| \hat{H} |i(0)\rangle
\]

(2.1)

where

\[
\omega_{fi} = (\varepsilon_{f}^{(0)} - \varepsilon_{i}^{(0)})/\hbar
\]

(2.2)

and \( \varepsilon_{i}^{(0)} \) and \( \varepsilon_{f}^{(0)} \) are the energies of the initial and final states respectively. We assume that the full Hamiltonian of an atomic system interacting with an electromagnetic field can be partitioned as

\[
\hat{H} = \hat{H}_0 + \hat{H}_1
\]

(2.3)

where \( \hat{H}_0 \) is the sum of the Hamiltonian of the electromagnetic field and that of the unperturbed atomic system, while \( \hat{H}_1 \), governing the interaction of the atomic system with the electromagnetic field [26], is given by

\[
\hat{H}_1 = \frac{e}{m_e c} \hat{A} \frac{i}{\hbar} \nabla + \frac{e^2}{2m_e c^2} \hat{A}^2
\]

(2.4)

where the vector potential operator \( \hat{A} \), characterizing the electromagnetic field in the case of a plane electromagnetic wave of wave vector \( \mathbf{k} \), unit x-ray polarization vector \( \mathbf{e}_p \) and frequency \( \omega_k \), is given by

\[
\hat{A} = \sqrt{\frac{\hbar}{2\omega_k V \varepsilon_0}} \left[ \hat{a}_{k,p} \mathbf{e}_p e^{i(k \cdot r)} + \hat{a}_{k,p}^\dagger \mathbf{e}_p e^{-i(k \cdot r)} \right]
\]

(2.5)

where \( V \) is an arbitrarily large normalization volume [27]. \( \hat{A} \) changes the number of photons by \( \pm 1 \). The second term of (2.4) will thus not contribute to absorption or emission of photons to first order. Furthermore, only the first term in (2.5)
gives absorption of photons (the second term gives emission). We also recognize the momentum operator \( \hat{\mathbf{p}} = \frac{\hbar}{i} \nabla \) in (2.4), and write for the interaction Hamiltonian

\[
\hat{H}_1 = -\frac{1}{\hbar^2} \frac{e}{m_e c} \sqrt{\frac{\hbar}{2\omega_k V\epsilon_0}} \left[ \hat{a}_{k,p} \hat{\mathbf{p}} \cdot \mathbf{e}_p e^{i(k \cdot r)} \right] \tag{2.6}
\]

Using (2.6) in (2.1), taking also the square modulus of the expansion coefficient to obtain the probability of finding the system in state \( |f⟩ \) after time \( t \), and performing the integration yields

\[
|c_{fi}(t)|^2 \propto \left| \frac{e^{i\omega_f t} - 1}{i\omega_f} \right|^2 \left| \left\langle f(0) | \hat{a}_{k,p} \hat{\mathbf{p}} \cdot \mathbf{e}_p e^{i(k \cdot r)} | i(0) \right\rangle \right|^2 \tag{2.7}
\]

The initial state \( |i(0)⟩ \) can be represented as a product state of an electronic \( |a⟩ \) and a photon state \( |n_{k,p}⟩ \)

\[
|i(0)⟩ = |a⟩ |n_{k,p}⟩ \tag{2.8}
\]

and similarly for the final state

\[
f(0)⟩ = |b⟩ |n_{k,p} - 1⟩ \tag{2.9}
\]

where one photon has been absorbed. The energy of the initial and final states are then given respectively by

\[
\epsilon_i^{(0)} = E_a + \hbar \omega_k \ n_{k,p} \tag{2.10}
\]

and

\[
\epsilon_f^{(0)} = E_b + \hbar \omega_k \ (n_{k,p} - 1) \tag{2.11}
\]

where \( E_a \) and \( E_b \) are the energies of the initial and final electronic states respectively.

It is possible to rewrite eqn. (2.7)\(^2\) and obtain for the transition probability per unit time [25] (normalizing to the number of incoming photons and omitting constants):

\[
\sigma_{fi} \propto \delta(E_b - E_a - \hbar \omega_k) \left| \left\langle b | \hat{\mathbf{p}} \cdot \mathbf{e}_p e^{i(k \cdot r)} | a \right\rangle \right|^2 \tag{2.12}
\]

This equation, often referred to as Fermi’s “golden rule” [28], will be the starting point for further approximations.

\(^2\)This is a quite lengthy exercise that can not be dealt with in detail here. From refs. [26] and [27]: use the relation \( \frac{e^{i\omega_f t} - 1}{i\omega_f} = \frac{e^{i(\omega_f t/2)} - 1}{i\omega_f/2} \cdot \sin \left( \frac{\omega_f t/2}{2} \right) = \frac{4\sin^2(\omega_f t/2)}{\omega_f^2} \) and identify the Dirac delta function \( \delta(\omega_f) = \lim_{t \to \infty} \frac{2\sin^2(\omega_f t/2)}{\omega_f^2} \). Plug this in, with the expressions for the total wave functions (2.8) and (2.9), and the energies (2.10) and (2.11), in eqn. (2.7).
2.1.1 The Dipole Approximation

Let us turn our attention to the matrix element appearing in eqn. 2.12.

\[ D_{ba} = \langle b | \hat{p} \cdot e_p e^{i(k \cdot r)} | a \rangle \]  \hspace{1cm} (2.13)

The exponential in (2.13) can be expanded in a Taylor series

\[ e^{i(k \cdot r)} = 1 + i(k \cdot r) + \frac{1}{2} (i(k \cdot r))^2 \ldots \] \hspace{1cm} (2.14)

If \( k \cdot r \ll 1 \) or equivalently, if \( |r| \ll \lambda/(2\pi) \) where \( \lambda \) is the x-ray wavelength, we can to a good approximation retain only the first term in the expansion (2.14) and obtain for the matrix element (2.13) the much simplified expression

\[ D_{ba} = \langle b | \hat{p} \cdot e_p | a \rangle = e_p \cdot \langle b | \hat{p} | a \rangle \] \hspace{1cm} (2.15)

known as the dipole approximation [28]. Following Stöhr [28] we can estimate the validity of employing the dipole approximation when calculating XAS at the oxygen K-edge. We then approximate \( |r| \) with the K-shell diameter from the Bohr radius \( a_0 = 0.53\text{Å} \) and the atomic number \( Z \) [28] as \( |r| \approx \frac{2a_0}{Z} \). With a photon energy \( \hbar \omega \approx 545\text{eV} \) we have the wavelength \( \lambda = 22.75\text{Å} \) and the condition \( |r| \ll \lambda/(2\pi) \) for the dipole approximation to be valid is well satisfied with 0.13 \( \ll 3.62 \).

The commutation relation

\[ \hat{p} = \frac{i m_e}{\hbar} [\hat{H}, \hat{r}] \] \hspace{1cm} (2.16)

can be used to rewrite eqn. 2.15 from its “velocity” form to its “length” form as

\[ e_p \cdot \langle b | \hat{p} | a \rangle = \frac{\omega k m_e}{\hbar} e_p \langle b | e \hat{r} | a \rangle \] \hspace{1cm} (2.17)

This is strictly valid only if the initial and final states \(|a\rangle\) and \(|b\rangle\) are exact eigenstates of the full Hamiltonian (2.3), although in practice only minor differences are observed using either expression in DFT. For Hartree-Fock calculations however, the difference may be significant [29]. It is the “length” form (i.e. right hand side of eqn. 2.17) which is used for the spectrum calculations with the StoBe [30] and GPAW [31] codes in Papers I, II, IV and V.

2.2 Density Functional Theory (DFT)

The basic idea behind DFT is to replace the use of a many-electron wave function \( \Psi(x_1, x_2, \ldots, x_N) \) having 3\( N \) degrees of freedom, with the much simpler electron density \( n(r) \), in electronic structure calculations. Already in the late 1920s Thomas and Fermi formulated a density functional theory for quantum systems [32, 33]. DFT was however widely ignored in the field of quantum chemistry until the late 1960’s [34]. Through the work of Hohenberg and Kohn [35] and that of Kohn and Sham [36] in 1965, for which Walter Kohn was later on awarded the Noble Prize in Chemistry 1998, DFT got a solid theoretical foundation and an SCF-like formulation. However,
2.2. DENSITY FUNCTIONAL THEORY (DFT)

It took almost three more decades before DFT reached its popularity among quantum chemists with the introduction of the now extremely popular hybrid functionals [37].

This section aims at giving a short introduction to the subject of Kohn-Sham DFT enough to appreciate the following section on spectrum calculations. A more in-depth description can be found in e.g. the book by Yang and Parr [38], or in any other quantum chemistry textbook such as the ESQC books [34]. A good introduction to DFT from a solid state perspective can be found in the book by Martin [39].

2.2.1 Background Definitions

We will here approach the subject of DFT from the viewpoint of wave function theory. Being interested in the physics of atoms and molecules (and for us water in particular), we can use the Born-Oppenheimer approximation [40] to separate nuclear and electronic motion

$$|\Psi_{full}(\mathbf{r}, \mathbf{R})\rangle = |\Psi(\mathbf{r}; \mathbf{R})\rangle |\Psi_{nuc}(\mathbf{R})\rangle$$

(2.18)

$$\hat{H}_{full} = \hat{H} + \hat{H}_{nuc}$$

(2.19)

where $\mathbf{r}$ and $\mathbf{R}$ are the electronic and nuclear coordinates respectively. The electronic wave function then only depends parametrically on the nuclear coordinates. By specifying the positions and charges of the nuclei one can solve separately the Schrödinger equation for the electronic part (2.20), where $|\Psi\rangle$, $\hat{H}$ and $E$ denote the electronic wave function, Hamiltonian and energy eigenvalue respectively.

$$\hat{H} |\Psi\rangle = E |\Psi\rangle$$

(2.20)

The non-relativistic Hamiltonian of a many-electron interacting system in the external potential from the nuclei can be written

$$\hat{H} = \hat{T} + \hat{U} + \hat{V}$$

(2.21)

where we have for the kinetic energy operator

$$\hat{T} = -\left(\frac{\hbar^2}{2m_e}\right) \sum_i \nabla_i^2$$

(2.22)

the electron-electron interaction

$$\hat{U} = \frac{e^2}{4\pi\varepsilon_0} \sum_i \sum_{j>i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

(2.23)

and the electron-nucleus interaction, i.e. the interaction of the electrons with the external potential

$$\hat{V} = \sum_i v(\mathbf{r}_i)$$

(2.24)

Taking $|\Psi\rangle$ to be normalized to unity, i.e. $\langle\Psi|\Psi\rangle = 1$ the expectation value of the energy is

$$E = \langle\Psi|\hat{H}|\Psi\rangle = \langle\Psi|\hat{T}|\Psi\rangle + \langle\Psi|\hat{U}|\Psi\rangle + \langle\Psi|\hat{V}|\Psi\rangle$$

(2.25)
The variational principle (see e.g. [25] p. 58) states that the wave function which minimizes the energy expression (2.25) is the ground state wave function (with the corresponding ground state energy). To find the first excited state, $|\Psi_1\rangle$, the energy is minimized with the constraint that the solution is orthogonal to the ground state. In general, if all $n-1$ states lower in energy are known, the $n$:th state can be found by minimizing the energy, with the additional constraint that

$$
\langle \Psi_m | \Psi_n \rangle = 0 \text{ for } m = 1, 2, \ldots, n - 1 \quad \text{and} \quad \langle \Psi_n | \Psi_n \rangle = 1
$$

(2.26)

The electron density $n(r)$, defined as the number of electrons per unit volume at the point $r$ in space, is connected to the many-particle wave function through the integral

$$
n(r) = N \int |\Psi(r_\sigma, x_2, \ldots, x_N)|^2 d\sigma_1 dx_2 \cdots dx_N
$$

(2.27)

where $x$ is taken to include both spin, $\sigma$, and space, $r$, coordinates. Using (2.27), we can write the last term in (2.25) as a functional of the density (see e.g. [39] p. 54).

$$
\langle \Psi | \hat{V} | \Psi \rangle = \int \Psi^* \left[ \sum_i v(r_i) \right] \Psi d\sigma_1 \cdots d\sigma_N = \frac{1}{N} \sum_i \int n(r_i)v(r_i)dr_i = \int n(r)v(r)dr
$$

(2.28)

### 2.2.2 The Hohenberg-Kohn Theorems

Hohenberg and Kohn presented in their work from 1965 two fundamental theorems for DFT [35].

Theorem I states that the external potential $v(r)$ is a unique functional of the density $n(r)$, apart from a trivial constant, given that the Hamiltonian is of the form (2.21). Since $v(r)$ fixes $\hat{H}$, the full many-particle (non-degenerate) ground state is a unique functional of the density $n(r)$.

Hohenberg and Kohn proved their Theorem I in the case of a non-degenerate ground state. It is however not necessary to restrict the validity of Theorem I to non-degenerate states (see discussion and references in [39] p. 123). Furthermore, the only ground state property of the wave function used in the proof is that it is the variationally lowest state. But we know from quantum mechanics that the variational principle can be subject to further symmetry etc. constraints; so if we can define a “variationally lowest” excited state, we could try to use Theorem I on that kind of state. The validity of such an approach is not easily proven but we can still go on with the calculations on a pragmatic basis (see e.g. [39] p. 198).

Theorem II defines for the kinetic and interaction energy a universal (i.e. independent of $v(r)$) functional of the density $F[n(r)]$:

$$
F[n(r)] = \langle \Psi | \hat{T} + \hat{U} | \Psi \rangle
$$

(2.29)
and states that for a given external potential \( v(\mathbf{r}) \) there exists a variational principle such that minimizing the total energy functional

\[
E[n(\mathbf{r})] = F[n(\mathbf{r})] + \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r}
\]

(2.30)

with respect to the density, subject to the constraint that the number of particles \( N \) is kept constant i.e. \( \int n(\mathbf{r})d\mathbf{r} = N \), yields the correct many-body ground state energy and density.

### 2.2.3 A Single-Determinant Wave Function

Electrons are fermions. That is, they must be described by an anti-symmetrical wave function, where interchange of two particles results in change of sign of the wave function (see e.g. [25] pp. 228). The total wave function of a collection of fermions \( \{x_i\} \) which are non-interacting, or interacting with each other only in a mean-field sense, takes the form of an antisymmetric product of one particle wave functions \( \{\chi_i\} \). This wave function, for an \( N \) particle system, is most conveniently written in the form of a determinant

\[
|\Psi_{SD}\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\chi_1(x_1) & \chi_2(x_1) & \cdots & \chi_N(x_1) \\
\chi_1(x_2) & \chi_2(x_2) & \cdots & \chi_N(x_2) \\
\vdots & \vdots & \ddots & \vdots \\
\chi_1(x_N) & \chi_2(x_N) & \cdots & \chi_N(x_N)
\end{vmatrix}
\]

(2.31)

known as a Slater determinant. The Pauli principle is built into a wave function of this kind. No two electrons can have all quantum numbers the same, i.e. occupy the same quantum state. Having two electrons in the same state corresponds to two equal columns in the determinant, which makes it vanish.

In the Hartree-Fock (HF) approximation [41, 42] the total wave function is taken on the form of a single Slater determinant and electron-electron interactions are treated in a mean-field approximation. The difference between the exact energy and the HF energy is defined as correlation energy [43]. The HF approximation makes up the very foundation of quantum chemistry, where the main concern for method development has been the introduction of electron correlation, which can be included either in a perturbative manner [44], or by expanding the true many-particle wave function in a set of Slater determinants [45]. Since this thesis is however only concerned with DFT, we refer to the book of Szabo & Ostlund [43] for a good introductory text on wave function methods in quantum chemistry.

### 2.2.4 The Kohn-Sham Formulation of DFT

The Kohn-Sham formalism [36] builds on the ansatz [39] that the density of a fully interacting many-electron problem can be described by some auxiliary system of non-interacting electrons. The system of non-interacting electrons can then easily be solved in a HF-SCF like manner, yielding the exact density and energy of the fully interacting system (if only we knew the exchange-correlation functional below).

The Hohenberg-Kohn functional (2.29) can be partitioned into the kinetic energy \( T_0[n(\mathbf{r})] \) and the classical Coulomb interaction \( J[n(\mathbf{r})] \) of the non-interacting
particles, and a “rest term”, the exchange-correlation functional $E_{xc}[n(r)]$:

$$F[n(r)] = T[n(r)] + U[n(r)] = T_0[n(r)] + J[n(r)] + E_{xc}[n(r)]$$

(2.32)

with

$$E_{xc}[n(r)] = (T[n(r)] - T_0[n(r)]) + (U[n(r)] - J[n(r)])$$

(2.33)

Introducing a set of Kohn-Sham orbitals $\{\phi^{KS}_i\}$ for the particles in the non-interacting system, makes it possible to write $T_0[n(r)]$ and the density $n(r)$ in terms of the Kohn-Sham orbitals (in atomic units):

$$T_0[n(r)] = -\frac{1}{2} \sum_i \langle \phi^{KS}_i | \nabla^2 | \phi^{KS}_i \rangle$$

(2.34)

and

$$n(r) = \sum_i |\phi^{KS}_i|^2$$

(2.35)

The Kohn-Sham orbitals will obey equations of the form

$$\hat{h}^{KS} \phi^{KS}_i = \epsilon_i \phi^{KS}_i$$

(2.36)

where

$$\hat{h}^{KS} = -\frac{1}{2} \nabla^2 + \hat{v}_{eff}(r)$$

(2.37)

The effective potential $v_{eff}(r)$ is given by

$$\hat{v}_{eff}(r) = v(r) + \int \frac{n(r')}{|r - r'|} dr + v_{xc}(r)$$

(2.38)

and the exchange-correlation potential is the functional derivative of the exchange-correlation energy functional (2.33)

$$v_{xc}(r) = \frac{\delta E_{xc}[n(r)]}{\delta n(r)}$$

(2.39)

The Kohn-Sham orbitals will then yield the exact density and energy of the fully interacting system, provided the exchange-correlation functional is known. In practice however, the exchange-correlation functional is not known. Even worse, there exists no known way to systematically improve upon an approximation for the functional. Regardless of the lack of an exact functional however, there are still good pragmatic reasons for using DFT. With the introduction of generalized gradient approximation (GGA) functionals [46] (such as PBE [47], BE88 [48] and BLYP [49]), and hybrid functionals such as the extremely popular B3LYP [37, 50] the accuracy of DFT calculations has approached that of wave function methods, but at a fraction of the cost.

### 2.3 Spectrum Calculations

In Papers I, II, IV and V in this thesis the XAS cross section is computed from eqn. (2.17), using the half core-hole transition potential (TP) DFT procedure [23],
where the same orbitals are used to represent the initial and final states, optimized in the StoBe-deMon code [30] (in Paper IV also with the TP-DFT implementation by Ljungberg et al. [51] in the GPAW code [31]) using half a core-hole in the oxygen 1s level. A brief account of the TP-DFT spectrum calculations, focusing particularly on the energy calibration, broadening, continuum representation and functional dependence, will be given below. Further discussions regarding these issues can be found in Paper IV.

### 2.3.1 The TP-DFT Approach to XAS

The localized character of the core orbitals makes it possible to define a variationally lowest first core-excited Kohn-Sham state by constraining the occupation number of the 1s Kohn-Sham orbital. Higher excited states are possible to reach by starting from the lowest excited state, removing the orbital containing the excited electron, adding an electron in the lowest unoccupied orbital and relax with the constraint of orthogonality against all other orbitals [52]. This state by state excitation procedure, known as the ΔKS or ΔSCF procedure, yields quite accurate relative energies between the excited states. Oscillator strengths can be obtained by taking the (somewhat involved) non-orthogonal matrix elements between the Kohn-Sham ground state determinant and each excited state determinant [53, 54]. This state by state procedure should give a fairly accurate description of XAS [52] however in practice only a few lowest states are accessible due to convergence and basis set limitations.

Slater devised a method to calculate transition probabilities, the transition state method [55], where the orbitals from the same reference state are used for both the initial and the final state. Taking the reference state to be at the transition between the ground and the excited state, with one half electron excited, it can be shown that relaxation is taken into account up to second order in a Taylor’s expansion of the energy [55] (see also discussion in Paper IV). Evaluation of the oscillator strengths becomes much simplified since the same orbitals are used to describe the final and initial state. The dipole transition moment eqn. (2.17) reduces to involve only the 1s and the excited electron Kohn-Sham orbitals.

The transition-potential approach in DFT (TP-DFT) introduced by Triguero et al. [23] avoids state-by-state calculations to obtain the spectrum simply by removing half an electron from the core-level of interest. The variationally relaxed density of the resulting molecular ion core then provides the potential from which the orbitals used for all excited states are obtained in one global diagonalisation (as opposed to one self-consistent calculation for each state). It is then enough to take the matrix elements between the Kohn-Sham orbitals corresponding to the 1s level and the unoccupied states to obtain the whole spectrum.

Although the use of a half core-hole in the TP-DFT calculations has a theoretical justification as an approximation to the Slater transition state method other core-hole occupations must sometimes be considered on a pragmatic basis. A discussion around different core-hole approximations for XAS calculations on liquid water and ice is given in Section 4.2.2.
2.3.2 Energy Calibration

For well ordered systems such as surface adsorbates [56] and smaller gas phase molecules [52] it is often sufficient to calculate XAS for one single geometry structure only; or a few geometries, e.g., in the case of different adsorption sites. The large variation in local structures in a molecular liquid however makes it important to calculate and sum together several hundred individual spectra to yield a total XAS spectrum. Using energy positions as obtained from a transition-potential spectrum calculation and shifting to experiment can be a valid procedure for a single geometric structure, but not when summing spectra from a large number of very different conformations of, e.g. water, where it is crucial to have the spectra correctly aligned on an accurate relative energy scale before summation. The same issue arises when excitations from non-equivalent atom centers are to be considered in a spectrum [57].

It is possible to obtain a reliable relative energy scale for spectra from individual water configurations using the $\Delta K S$ approach, where the difference in total energy between the ground state and the first excited state is computed for each configuration. The lowest energy state in the TP spectrum is then set equal to the $\Delta K S$ energy, and all other states are shifted accordingly [52, 58].

The absolute energy of the TP spectrum can be further corrected to within a few tenths of an eV from experiment by a computationally derived empirical shift for relativistic and functional dependent effects. The exchange-correlation functionals used in DFT are only approximate and therefore results may depend on which functional is used. The main contribution to this error is from the core level where the electron density is the highest [59]. It was shown in ref. [59] that this amounts to an overall shift of the spectrum, with little effect on energy differences between the states in the $\Delta K S$ corrected TP spectrum. It is therefore possible to correct for this deficiency by computing the core-electron binding energy (CEBE) as the total energy difference between the fully relaxed ground and core ionized states for the element and compound of interest, and compare this against the experimental value. The difference is then added as a constant shift to the whole TP spectrum. It is important here that the reference system used is similar enough to the system studied for the calibration procedure to be valid. Relativistic effects which come in also as a constant energy shift [59] (0.33 eV for the oxygen $K$-edge), as well as energy effects of a limited basis set etc., are automatically included in this empirical correction procedure. An illustrative example of the accuracy of the energy scale obtained using the $\Delta K S+\text{CEBE}$ procedure is given in Figure 4.11 for a gas phase water molecule.

2.3.3 Broadening

There are several sources of broadening in an experimental XAS spectrum. Typically there will be an intrinsic lifetime broadening, a vibrational and configurational broadening and a certain instrumental resolution. The weighting of each contribution will depend on the particular system, as well as on the particular experimental setup and instrumentation. The experimental instrumental resolution is Gaussian with a certain width depending on the experimental setup. The life-time broadening is Lorentzian with a full width at half maximum (FWHM) of 0.18 eV at the oxygen...
K-edge [60]. Going to higher energies gives a shorter life-time and therefore a larger broadening.

The vibrational broadening is typically inhomogeneous and depends generally on the vibrational wave functions in both the electronic ground and excited states [52], while configurational broadening can be pictured as a summation over inequivalent atomic centra of the same element in the sample. In the case of a molecular liquid, such as water there will be molecules in different geometrical configurations giving rise to different spectra; the mean spectrum from different local structures will in general not be equal to the spectrum from the mean geometry. We shall see in Section 4.2.1 below that the vibrational broadening can be thought of as a configurational averaging over the zero-point probability distribution, in the case when the excited states are strongly anti-bonding.

A theoretical TP XAS spectrum consists of a set of discrete energy positions with associated oscillator strengths. To be able to communicate and compare against experimental results it is thus necessary to account for the broadening also in the theoretical spectra. The most straightforward way is to simply apply a constant Gaussian broadening to all discrete peaks in the spectrum. This treatment is often enough to compare the near-edge spectral features with experiment. To go slightly higher in energy the \textit{ad hoc} procedure of applying a broadening with linearly increasing width is often favored. Such a broadening scheme, if applied correctly, can give an improved description of the high-energy part of the near-edge spectrum, mostly because it can cover up some basis set related artifacts (Section 2.3.4 below), without affecting the overall intensity distribution. A broadening of this type is used in Papers I and II, and further investigated and compared to a constant Gaussian broadening in Paper IV.

Applying a Gaussian broadening to the discrete spectrum can be a valid procedure to account for life-time broadening and instrumental resolution, however for treatment of configurational broadening great caution must be exercised. It was shown in the supplementary online material to ref. [6] that small distortions around a mean geometry can be reliably accounted for using a Gaussian broadening on the spectrum taken at the mean geometry. It is however unlikely that the same would be true for different more distorted geometrical configurations in a liquid. The need for a proper configurational averaging when computing spectra from a disordered structure is further discussed in Section 4.2.1 below.

A broadening scheme applied to a theoretical spectrum must be chosen with great care. Most importantly the broadening must be stable, in the sense that conclusions drawn from the theoretical spectrum must be to a large extent unaffected by the particular choice of broadening. Paper IV gives a longer discussion about different proposed broadening schemes for liquid water. As a rule of thumb the broadening should, if possible, be used to mimic only life-time effects and instrumental resolution, unless the other sources of broadening in the experiment are already well known.

\section{Continuum Description}

The TP-DFT spectra are obtained with the StoBe code [30] using a double basis set procedure [61, 62], in which the basis set is augmented with extra diffuse functions after convergence of the half core-hole calculation. The KS matrix is then diagonal-
ized again in this larger basis to obtain the unoccupied orbitals used for calculating transition probabilities. The description of the unoccupied states will inevitably start to fail at some energy. The wave function of an ejected photo-electron going off to infinity as a spherical wave can of course not be captured correctly using a finite localized basis set. The problem of handling the continuum is thus inherent in the localized basis set approach.

![Figure 2.1](image_url)

**Figure 2.1:** (a) Computed gas phase water spectrum (full line) broadened up to 4.25 eV in the continuum using the standard augmentation basis on the oxygen, and (b) the same spectrum obtained using the standard augmentation basis on the oxygen, as well as on 9 different dummy centers corresponding to the oxygen positions of an ice Ih lattice, using the same broadening. The vertical bars are the computed oscillator strengths at their computed energies. The experimental curve (dotted line) [63] is included for reference.

Figure 2.1 (a) shows the computed spectrum of a gas phase water molecule in its equilibrium geometry broadened up to 4.25 eV in the continuum using the standard augmentation basis of 19 extra diffuse $s$, $p$ and $d$ functions (i.e. totally 171 extra functions). The experimental spectrum [63] is also shown (dashed line), as well as the distribution of computed oscillator strengths (vertical bars). It is obvious that the basis set description starts to fail already below 545 eV. The oscillations in the broadened spectrum which increases in amplitude with higher energy is a clear sign of basis set artifacts.

For the spectrum in Figure 2.1 (b) the same broadening as in (a) was applied, but using a much larger augmentation basis. The standard augmentation basis set was placed on 9 dummy centers in a fictive ice lattice around the central molecule, thus giving a total of 1710 extra diffuse functions. The artifacts seen in Figure 2.1 (a) are no longer present. Instead a smooth representation of the continuum in good agreement with the experimental curve is found. Clearly it is possible to improve
2.3. SPECTRUM CALCULATIONS

Figure 2.2: Functional dependence of the computed XAS spectrum for a specific 11-molecules cluster using combinations of the PBE [47] functional for exchange with all in the StoBe code [30] available functionals for correlation, as well as all available functionals for exchange combined with the PBE functional for correlation. Top spectra use the energy scale as it comes out of the HCH TP-DFT calculation; the middle spectra have been $\Delta K_S$ shifted to account for relaxation effects; the bottom spectra have been shifted also according to the CEBE empirical functional correction.

on the continuum representation simply by adding more basis functions, although it should be noted that this does not solve the problem, but rather pushes it further up in energy. It is therefore highly important to use a sufficiently large augmentation basis set in the spectrum calculations to adequately describe the particular energy region of interest. One otherwise runs the risk of drawing conclusions based on pure artifacts, as e.g., the “bare OH$^-$” spectrum in ref. [64] illustrates only too well.

If interested in the X-ray absorption at higher energies than the immediate near-edge region within about 15 eV from the edge some alternative approach must be considered. The TP-DFT implementation in GPAW [51] is one such alternative. This code is particularly useful for calculating large bulk systems because of the efficient parallelization possible using the real space grid representation of the wave function. The grid representation furthermore allows for accurate calculations in the continuum where a local basis set description breaks down. Also real space full multiple-scattering (RSFMS) calculations using the FEPF code [65] have been successfully applied to ice in the low energy continuum region [66].

Going to even higher energies into the EXAFS region, the multiple-scattering approach is the only natural choice.

2.3.5 Functional Dependence

The energy calibration scheme outlined in Section 2.3.2 above was designed to also correct for functional dependence of the spectrum energy position through the CEBE shift. Figure 2.2 gives an indication of how well this works in practice by showing spectra of an 11 molecules water cluster calculated using combinations of the PBE functional [47] for exchange with all correlation functionals available in the StoBe code, as well as using all possible combinations of available exchange functionals with the PBE functional for correlation. This gives a total of 18 combinations in the figure. All spectra are broadened with a constant 0.5 eV FWHM Gaussian broadening to highlight any differences.
The topmost spectra are taken as they come out from the TP-DFT calculations, without considering further energy corrections. There is considerable spread in the energy position depending on functional. The middle spectra have been compensated for relaxation effects in the first excited state via the $\Delta KS$ procedure. The situation is improved, but the spectra still do not coincide perfectly in energy. The bottom spectra are treated with the full $\Delta KS+CEBE$ shifting procedure as described in Section 2.3.2 above. Indeed, the spectra now align quite well, so that the dependency of the energy scale on the choice of functional is highly reduced.

Although the energy scale is quite stable there are still small variations in the intensity distribution, particularly in the main-edge region, for the different functionals. This intensity difference is hard to compensate for, so if one has no particularly strong reason to believe in the performance of one functional over another, then conclusions should not be drawn which are not stable with change of functional. It is still important though, to use the full $\Delta KS+CEBE$ correction scheme to minimize the functional dependence of the final spectrum.
Chapter 3
Reverse Monte Carlo Simulations

Since first outlined by McGreevy and Pusztai in 1988 [67] Reverse Monte Carlo (RMC) has become a widespread tool for data analysis. The introduction of large three-dimensional structure models in the analysis of x-ray diffraction (XD) and neutron diffraction (ND) data has had an enormous impact on our understanding of disordered materials such as covalent glasses and molecular liquids and structure modeling with RMC has become a standard tool for diffraction analysis. With an underlying three-dimensional structure model to represent the data many insights can be obtained which would otherwise not be possible [68].

RMC has been used in Papers II and III (and in Paper I the related EPSR technique [69]) to test hypotheses regarding H-bonding topologies in liquid water against XD and ND data. This chapter will treat the most general aspects of RMC structure modeling of diffraction data and geometrical constraints for H-bonding. For a more complete picture of RMC and related techniques we refer to the review by McGreevy [70].

3.1 Metropolis Monte Carlo and the Reverse Monte Carlo Algorithm

Describing the Reverse Monte Carlo (RMC) algorithm is most easily done by first considering the Metropolis Monte Carlo (MMC) algorithm [71]. Given an expression for the potential surface of a system of particles as a function of the particle coordinates, $E(r)$, a trial-move $\Delta r$ of one or more particles is made and the change in energy due to the move is computed as

$$\Delta E = E(r + \Delta r) - E(r)$$  \hspace{1cm} (3.1)

A move with $\Delta E \leq 0$ is always accepted. If a move generates an increase in energy, i.e. if $\Delta E > 0$, the move is accepted or rejected according to a Boltzmann type criterion

$$\text{accept if } \text{rnd}[0,1] \leq e^{-\Delta E/k_B T}$$  \hspace{1cm} (3.2)
 reject if \( \text{rnd}[0,1] > e^{-\Delta E/k_BT} \) \hspace{1cm} (3.3)

where \( \text{rnd}[0,1] \) is a random number between 0 and 1. If a move is rejected the last accepted configuration is stored as the new one. The configuration space of the system is in this way probed according to a Markov-chain importance sampling, where snapshots can after equilibrating be sampled to yield thermodynamical averages in a chosen thermodynamical ensemble [9].

Algorithmically the RMC procedure [67] is identical to the above described MMC. But what is given at first, rather than a potential, is a reference set of data \( f_r \), of some quantity that can also be calculated from the coordinates of the particles in the simulation, \( f_c(r) \). An error function \( \chi \) is defined as

\[
\chi^2(r) = \sum_i \left( \frac{f_{c,i}(r) - f_{r,i}}{\sigma_i} \right)^2
\]

(3.4)

where the sum is over all data points and \( \sigma_i \) is a parameter giving the weight of the fit in point \( i \). If \( f_c \) is a set of experimental data and the experimental uncertainty is known \( \sigma_i \) could be set in the fit to that value. Otherwise, as is most often the case, \( \sigma_i \) is treated as a free parameter chosen to give a reasonably hard fit to the provided reference data. Using now \( \Delta \chi^2 \) instead of \( \Delta E \), defined as

\[
\Delta \chi^2 = \chi^2(r + \Delta r) - \chi^2(r)
\]

(3.5)

the acceptance criterion for moves with \( \chi^2 > 0 \) is written as

accept if \( \text{rnd}[0,1] \leq e^{-\Delta \chi^2} \) \hspace{1cm} (3.6)

\[
\text{reject if } \text{rnd}[0,1] > e^{-\Delta \chi^2}
\]

(3.7)

still accepting all moves with \( \chi^2 \leq 0 \). Thus \( \sigma_i^2 \) takes the place of the temperature in conventional MMC, while the squared difference between computed and reference data takes that of the energy.

### 3.2 Diffraction Data and Geometrical Constraints

The reverse nature of RMC (connected to the inverse problem of finding an interaction potential, \( v(r) \), from a PCF [72]) becomes apparent when fitting diffraction data. Diffraction data is rather directly connected to the pair-correlation functions (see section 3.2.1 below). The pair-correlation functions in turn, assuming pairwise additive forces, determine the potential (see ref. [72] and references therein). So in principle, for simple pairwise additive systems diffraction data as input yield the potential governing the forces between the particles; this corresponds to the potential which would be used in a MMC simulation to obtain thermodynamical information.

Reality is never that simple however. Uniqueness in the fitting is as a rule never achieved. Few real systems are described accurately enough using pair-wise additive forces only. Simulation boxes are of finite size and diffraction data have limited \( Q \)-range. Using the best available data and a clever choice of fitting parameters in conjunction with geometrical constraints, however, still makes it possible to learn a lot about the particular system of interest.
3.2. DIFFRACTION DATA AND GEOMETRICAL CONSTRAINTS

3.2.1 X-Ray Diffraction (XD) and Neutron Diffraction (ND)

The x-ray and neutron diffraction patterns are calculated in RMC via the partial structure factors (PSFs) obtained by Fourier transforming the pair-correlation functions $g_{\alpha\beta}(r)$

$$A_{\alpha\beta}(Q) = 1 + 4\pi \rho \int r^2 (g_{\alpha\beta}(r) - 1) \frac{\sin(Qr)}{Qr} dr$$  \hspace{1cm} (3.8)

where $\rho$ is the atomic number density. The total structure factors are then formed as linear combinations of the PSFs, weighted together in the case of ND with the atomic scattering lengths $b_i$, and for the XD signal using $Q$-dependent atomic form factors $f_i(Q)$,

$$S_{ND}(Q) = \sum_{\alpha} \sum_{\beta} (2 - \delta_{\alpha\beta}) c_\alpha c_\beta \langle b_\alpha \rangle \langle b_\beta \rangle (A_{\alpha\beta}(Q) - 1)$$  \hspace{1cm} (3.9)

$$S_{XD}(Q) = \sum_{\alpha} \sum_{\beta} (2 - \delta_{\alpha\beta}) c_\alpha c_\beta f_\alpha(Q)f_\beta(Q) (A_{\alpha\beta}(Q) - 1)$$  \hspace{1cm} (3.10)

where $c_i$ is the concentration of the $i$:th atom type, the Kronecker delta function $\delta_{\alpha\beta}$ is to prevent double counting and the angular brackets denote spin and isotope averages. The neutron scattering lengths can be found in standard tables [73] and the x-ray atomic form factors are calculated at the required $Q$-values using an analytical five Gaussian fit [74] to accurate Dirac-Fock calculations [73]. While neutrons scatter from the atomic nuclei, hence the element and isotope specific scattering lengths $b_i$, x-rays scatter from the electrons. The atomic form factor $f_\alpha(Q)$ is related to the electron density $\rho_\alpha(r)$ associated with atom $\alpha$, through a Fourier transform.

Electron density is transferred from the hydrogens to the oxygen when forming chemical bonds in the water molecule. To account for this charge transfer in the description of the atomic form factors, Sorensen et al. [19] introduced modified atomic form factors (MAFFs)

$$f'_i(Q) = \left[1 + \alpha_i \exp \left(-\frac{Q^2}{2\delta_i^2}\right)\right] f_i(Q)$$  \hspace{1cm} (3.11)

obtained through altering the independent atomic form factor $f(Q)$ at lower values of momentum transfer, while leaving the higher $Q$ part intact. This reflects that core electrons, which dominate $f(Q)$ at higher $Q$, are rather unaffected by chemical bonding. $\alpha_i$ is here a scaling factor giving the redistribution of charge and $\delta_i$ represents the extent of valence electron delocalization due to the chemical bond. For the RMC simulations in Papers II and III, $\alpha$ was set to correspond to the transfer of 0.4 electrons from each hydrogen atom to the oxygen atom, with the total number of electrons per molecule kept constant. The estimated gas phase value of 2.2 [19] was used for $\delta$. Although the MAFFs do not exactly reproduce the molecular form factor of water from e.g. Wang et al. [75], a significant improvement is expected compared to using the independent atomic form factors.

Distances are calculated and stored in a histogram representation of $g_{\alpha\beta}(r)$, taken to $Q$-space via the Fourier transform equation (3.8) and combined to total structure factors using equations (3.9) and (3.10), at the start up of a typical RMC simulation.
modeling diffraction. The $\chi^2$ value from fitting diffraction is set up according to

$$\chi^2_D = \sum_{i,q} \left( \frac{S^{(rmc)}_{i,q} - S^{(ref)}_{i,q}}{\sigma_{i,q}} \right)^2$$

for all datasets $i$, and $Q$-values, $q$; where $S^{(ref)}$ is a reference data set, and $\sigma_{i,q}$ is the weighting factor for the particular $Q$-value and data set, $i$. At each trial move, the change in $\chi^2_D$ due to the move is recorded and added to the global $\chi^2$ value for evaluation of the acceptance criteria eqns. (3.6, 3.7).

### 3.2.2 Geometrical Constraints

It is possible to run an RMC simulation with no further constraints on the structure except to fit the provided reference data. The main advantage however, with a technique relying on a set of coordinates for the interpretation of the data, is the possibility of imposing geometrical constraints on the structural solution. Preventing atomic overlap is a first, maybe too obvious although extremely important, constraint that should always be applied. Simply rejecting moves where two atoms get in close vicinity of each other can give a great deal of information about possible errors in the data. Diffraction data sets which cannot be fitted within reasonable error bars in RMC with no further constraints, even with small atomic cutoff radii, can not be considered physically meaningful [76] and are probably subject to systematic errors.

The highly averaged nature of the diffraction data makes it possible to fit the diffraction signal from a molecular liquid such as water without having molecules defined in the simulation box; two parts of hydrogen atoms and one part oxygen will do. Having water molecules defined is however necessary if we want to draw any meaningful conclusion concerning real water. Holding molecules together is often done via fixed neighbor constraints (FNCs), where specific atoms are grouped together, representing chemical bonds with fixed interval cutoffs. This representation of molecules is usually considered enough for modeling diffraction data. For use in conjunction with H-bond constraints however (Section 3.4 below) more detailed control over the intramolecular angles and distances is needed. If the resulting structures from the RMC simulation are to be used in spectrum calculations it is also important that the distribution of molecular geometries gives a realistic sampling of the zero-point vibrations.

It is possible to impose a wide range of geometrical constraints in RMC where constraints for H-bonding is just one example. Other implemented and often used geometrical constraints include the average coordination constraints, generalized coordination number constraints and cosine bond angle constraints [77].

### 3.3 Empirical Potential Structure Refinement

Empirical Potential Structure Refinement (EPSR) [69] is a technique similar to RMC in that it uses a Monte-Carlo approach with an underlying structure model to extract structural information from diffraction data. While RMC relies as much as possible on the information content in the data modeled, adding geometrical constraints to
3.4. H-BONDS IN RMC

conform to known physics when lacking sufficient information from the data, EPSR takes the opposite approach. The idea behind EPSR is to build in as much physics as possible when fitting the diffraction data, through the use of a reference potential, to guide the structure toward a physically sound solution [78, 21].

In its original formulation [69] EPSR makes use of site-site pair-correlation function data sets $g_D^{\alpha\beta}(r)$ (as derived e.g. from neutron diffraction experiments [79]), to modify a reference potential $U_n^{\alpha\beta}(r)$ until the site-site pair-correlation functions from the potential in an MMC simulation $g_n^{\alpha\beta}(r)$ agree with $g_D^{\alpha\beta}(r)$.

After equilibrating in an MMC run, $g_n^{\alpha\beta}(r)$ is calculated from the simulation and the potential is updated according to

$$ U_{n+1}^{\alpha\beta}(r) = U_n^{\alpha\beta}(r) + kT \ln \left[ \frac{g_n^{\alpha\beta}(r)}{g_D^{\alpha\beta}(r)} \right] $$  (3.13)

This procedure is then repeated, assuming the procedure is convergent, until

$$ U_n^{\alpha\beta}(r) \approx U_{n+1}^{\alpha\beta}(r) = U_D^{\alpha\beta}(r) $$  (3.14)

and hence

$$ g_n^{\alpha\beta}(r) \approx g_D^{\alpha\beta}(r) $$  (3.15)

for all $r$ and all atom pairs $\alpha\beta$. Although extended in later work [80] to make use of a redundant set of structure factors, and to make the comparison against experiment directly in $Q$-space, the fundamental approach of EPSR described here remains the same; to iterate MMC simulations and update the reference potential with guidance from the fit to experiment, until the potential converges.

Formally, convergence of the EPSR procedure follows from a uniqueness theorem for the site-site pair-correlation function in pairwise additive systems, given an infinite simulation box [69]. Later work however, suggests that the initial choice of reference potential can strongly affect the final solution [81, 82]. This was most apparent in ref. [81] when XD and ND data on water was modeled using starting potentials with different charge asymmetry on the two hydrogens in an attempt to create asymmetric water structures [81]. Equal quality of the fits was obtained for all starting potentials, resulting in a series of very different structures, though all seemingly in agreement with the diffraction data.

3.4 H-bonds in RMC

Even though mostly diffraction data has been modeled traditionally in RMC [70] the general nature of the algorithm makes it possible to model all sorts of data which can be calculated from the coordinates of the particles [67]. For practical reasons however, there are limitations to what data can be modeled particularly because of the demand for computational speed. To be incorporated directly into the RMC algorithm a structural probe must be evaluated fast enough so that a sufficient number of configurations can be sampled during the simulation. With today’s available computer resources this unfortunately disqualifies the use of TP-DFT XAS calcu-
lations in RMC\textsuperscript{1}. To still test the validity of XAS-based conclusions regarding the H-bond topology of liquid water [6] against diffraction data, geometrical constraints for H-bonding were implemented in the RMC++ code [83] for use in Papers II and III.

An H-bonding cone was defined (as proposed in ref. [6]) as

\[ r_{OO} < r_{OO}^{\max} - \alpha \theta^2 \]  \hfill (3.16)

where \( r_{OO} \) is the O\(_1\)\( \cdots \)O\(_2\) distance in Å considered to give an intact H-bond, \( \theta \) is the H-O\(_1\)\( \cdots \)O\(_2\) angle (in degrees), where H is covalently bonded to O\(_1\) and forms a (possible) H-bond with O\(_2\), \( \alpha \) is a parameter giving the curvature of the cone and \( r_{OO}^{\max} \) gives the range of the cone at a straight angle (i.e. for \( \theta = 0 \)).

To define an H-bond in RMC, two H-bonding cones were used (similar to ref. [58]), replacing (3.16) with (3.17) and (3.18), defining a strictly bonding O\(_1\)-H\( \cdots \)O\(_2\) as

\[ r_{OO} < r_{OO}^{\text{inner}} - \alpha \theta^2 \]  \hfill (3.17)

and a strictly broken bond as

\[ r_{OO} > r_{OO}^{\text{outer}} - \alpha \theta^2 \]  \hfill (3.18)

The implementation was made with the possibility of future use for other H-bonded systems in mind, thus keeping the code as general as possible, with no hard coded features specific to water. Instead, the number of cones, and for each cone all cone parameters \( r_{OO}^{\text{inner}}, r_{OO}^{\text{outer}} \) and \( \alpha \) as well as target “concentrations” together with corresponding \( \sigma \) parameters, are fed to the program as input at runtime.

Which atom types to treat as H-bond donors and H-bond acceptors is also given at runtime. When the program starts, the H-bonding situation for each atom of acceptor type is registered\textsuperscript{2}. The number of acceptors in each H-bonding (HB) situation is summed together, and the fraction of acceptors \( f_{HB,ij} \) in each particular HB-situation, \( i \), is stored for each HB-cone, \( j \), consisting of an inner and outer boundary as described above.

The contribution to the total error function \( \chi^2 \) from the set of HB-constraints, \( f_{HB,ij} \) is evaluated according to (3.19), where \( f_{r,ij} \) is the target “concentration” for the \( i \)th HB-constraint and the \( j \)th cone, and \( \sigma_{ij} \) is the corresponding weighting factor.

\[ \chi^2_{HB} = \sum_i \sum_j \left( \frac{f_{HB,ij} - f_{r,ij}}{\sigma_{ij}} \right)^2 \]  \hfill (3.19)

The change in \( \chi^2_{HB} \) due to the move is evaluated and the value is added to the global \( \chi^2 \) in the simulation before the acceptance test is performed.

The H-bonding constraints were found impossible to use efficiently unless any two water molecules were prevented from mutually donating and accepting H-bonds with each other. Trying to maximize the H-bond connectivity otherwise almost

\textsuperscript{1}To overcome this obstacle the SpecSwap-RMC procedure (Section 4.3) was developed in Paper V.

\textsuperscript{2}When an acceptor is said to be in e.g. DD (Double Donor) situation, it is understood that two of the acceptor atom’s covalently bonded donors are involved in H-bonding.
3.4. H-BONDS IN RMC

immediately results in the RMC simulation getting trapped in a local minimum, with pairs of water molecules binding to each other. Situations with one acceptor donating an H-bond, through one of its covalently bonded donors, to another acceptor, and at the same time accepting an H-bond from a donor covalently bonded to that other acceptor was therefore also counted and treated as an H-bond data point (named PP) among the others (ND, SD, DD, etc.) and fitted simultaneously with a large weight (small \( \sigma \)) against zero such PP interactions.

3.4.1 Covalent Bonds and Internal Geometries

Since a large fraction of the total neutron structure factors is due to intramolecular scattering (see the discussion in Paper III), a good fit to the data requires allowed variations in the internal O-H distances and H-O-H angles as large as in the real liquid, i.e. including quantum zero-point vibrational effects on the distribution of distances and angles. FNCs are traditionally used to fix molecular connectivity in an otherwise atomic RMC run (see the RMCA manual [84]), with hard cutoffs for allowed bond distances. For the RMC simulations in Papers II and III, covalent O-H bonds were constrained to the interval \((0.79 - 1.17) \text{ Å}\), and internal H-H distances to \((1.0 - 2.0) \text{ Å}\).

Imposing constraints for H-bonding on top of the FNC constrained liquid can generate some peculiar unphysical behavior. In order to satisfy H-bond constraints, the internal geometries may distort within the given FNCs; in particular, the first attempt to minimize the number of H-bonds in Paper II resulted in almost straight H-O-H angles. RMC has a tremendous power to go the shortest way to satisfy a constraint. Since the other data sets used in the fit did not put hard enough constraints on internal geometries, the easiest way to break a large number of H-bonds turned out to be by making the water molecules almost linear.

This kind of behavior forced an implementation of more precise internal geometry control. Histograms were set up with all internal distances and angles, and updated appropriately after each move. The changes in the histograms were recorded and comparisons were made against reference distribution histograms to compute values of \( \Delta \chi^2_{\text{bonds}} \) and \( \Delta \chi^2_{\text{angles}} \) for each move, to add to the global \( \Delta \chi^2 \) value. The reference distribution histograms used in Papers II and III were taken as Gaussians with approximately the same FWHM as distributions of O-H distances and H-O-H angles from a path integral simulation of water [85].

To prevent the internal geometries from distorting due to the H-bond constraints, the use of quite small \( \sigma \) values was found necessary. But a too small \( \sigma \) value freezes the structure, resulting in a very poor ratio of accepted/rejected moves. To overcome this, a series of \( \sigma \)'s were used, keeping a firm fit (with small \( \sigma \)) at the sides of the reference distributions while allowing for substantial deviations from the references near the mean geometry. In this way a significant speed-up of the fitting could be achieved while still keeping sufficient control over the intramolecular geometries.
Chapter 4

Summary of Main Results

The results in this thesis can be divided into three separate but related parts. In Papers I, II and III structure models of liquid water with different H-bond topologies, fitted to diffraction data using either EPSR or RMC simulations, are investigated in terms of diffraction, vibrational spectroscopy and XAS. Paper IV itself makes up a large and important part of this thesis, with its extensive overview of the TP-DFT XAS calculations on water in gas, liquid and solid phases. In Paper V we connect the RMC simulations with the spectrum calculations by introducing a new way to analyze data, the SpecSwap-RMC method. The method is subsequently applied to the study of EXAFS and diffraction on water in Paper VI.

4.1 Papers I, II and III

We start out in Paper I with an investigation of the XAS and IR/Raman spectra from a series of symmetric and asymmetric structure models of liquid water fitted to diffraction data using the EPSR technique. None of the investigated structure models reproduced the experimental XAS, and two different approaches to model IR/Raman spectroscopy gave contradicting results for the most asymmetric structure model. In Paper II the EPSR technique was abandoned in favor of RMC simulations. Two extreme structure models, with symmetric or asymmetric local H-bonding configurations, were created by means of geometrical constraints for H-bonding in RMC. Both XD and ND data were fitted, as well as the E-field distribution from an MD simulation as an approximation to the O-H stretch vibrational spectrum of dilute HOD in D₂O. It was shown that diffraction and IR/Raman data do not prove that water is a tetrahedrally connected liquid. In Paper III, XD and ND data was again fitted using RMC (but leaving out the E-field distribution), with and without constraints for H-bonding, and a detailed investigation of the information content in the diffraction data on liquid water was made.

Three main conclusions can be drawn on the basis of these papers. Firstly, that the available diffraction data put little constraints on the type of H-bond topology or O-O-O tetrahedrality in the structure. Secondly, that classical MD simulations, using some of the most common interaction potentials for water, give rise to O-O and O-H PCFs with too sharp first peaks at too short distances to be in agreement with
diffraction. Thirdly, that requiring a large fraction of broken H-bonds according to
the cone criterion of ref. [6] is not in itself enough to reproduce the experimental
XAS spectrum.

4.1.1 Analyzing EPSR Structures

The combined experimental and theoretical XAS study of Wernet et al. [6] has
proposed the number of H-bonds in liquid water to be close to two per molecule,
with emphasis on locally asymmetric configurations. This is in sharp contrast to
the conventionally accepted picture of water as having close to four H-bonds per
molecule in a distorted tetrahedral network. To test the proposed structure from
ref. [6] against XD and ND data a series of water structure models, ranging from
symmetric to very asymmetric local configurations of the water molecules, were
created using the EPSR technique [81]. It was found in ref. [81] that the whole range
of models could reproduce diffraction, despite differing widely in their local H-bond
environment. Paper I investigates the water structure models from ref. [81] in terms
of their computed XAS and IR/Raman spectra. Based on the conclusions from ref.
[6] one would expect the more asymmetric structure models to better reproduce
the experimental XAS. One could also anticipate the models with more broken or
weakened H-bonds to have IR/Raman spectra shifted to higher frequencies.

The asymmetric structure models in ref. [81] were obtained by altering the
charges on the hydrogens in the EPSR reference potential, by moving charge from
one hydrogen to the other on the same water molecule. It is important to empha-
size that this charge asymmetry was used only as a means to create asymmetric
local structures and not, as misinterpreted by some [86, 87], to actually represent
a proposed realistic scenario of charge asymmetry in the liquid. Table 4.1 shows
the charge parameters used for each reference potential, and the resulting number
of H-bonds per water molecule after the EPSR refinement, using the geometrical
H-bond definition from ref. [6]. There is a clear trend towards lower number of H-
bond with increasing charge asymmetry. It is important to realize however that the
coordination number, as defined by integrating the first peak in the O-O PCF, is
not significantly changed between the different models. The coordination number
of slightly more than four nearest neighbors is fairly well determined by the diffraction
data [11]. As a result of the EPSR simulation the change induced in the coordina-
tion around one hydrogen by the imposed charge asymmetry is compensated by a
change in the coordination shell around the other hydrogen, leaving the angularly
integrated coordination practically unchanged for all models.

<table>
<thead>
<tr>
<th>Model</th>
<th>q(O)</th>
<th>q(H1)</th>
<th>q(H2)</th>
<th>HB</th>
</tr>
</thead>
<tbody>
<tr>
<td>a2</td>
<td>-0.848</td>
<td>+0.424</td>
<td>0.424</td>
<td>2.9</td>
</tr>
<tr>
<td>a2,2</td>
<td>-0.810</td>
<td>+0.262</td>
<td>0.548</td>
<td>2.6</td>
</tr>
<tr>
<td>a2,3</td>
<td>-0.785</td>
<td>+0.207</td>
<td>0.578</td>
<td>2.5</td>
</tr>
<tr>
<td>a2,4</td>
<td>-0.680</td>
<td>+0.100</td>
<td>0.580</td>
<td>2.3</td>
</tr>
<tr>
<td>a2,6</td>
<td>-0.600</td>
<td>+0.000</td>
<td>0.600</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Table 4.1: Parameters for water models used in the EPSR refinement
in ref. [81]. q gives the charge of the
atomic species and HB gives the result-
ing average number of H-bonds using
the definition of ref. [6].
**XAS Analysis**

The computed XAS spectra for models a2, a2.4 and a2.6 are shown in Figure 4.1. The trend in the number of H-bonds for the models is to some extent reflected in the computed spectra. With increasing amount of asymmetrically distorted H-bonds, more intensity is shifted down in energy towards the onset of the spectrum. It is however immediately obvious that none of the models reproduce the experimental spectrum, not even on a qualitative level. This observed mismatch could be due to one or more of several sources of errors; errors in the experiment, errors in the calculations, or errors in the structure, i.e., that the structure models are not representative of water.

Measuring XAS on liquid water is a great experimental challenge\(^1\). However, after being re-measured numerous times over the last half decade or so, with different experimental setups and detection schemes, all measurements now agree very well on the shape of the spectrum and only minor differences persist between the most recent spectra [88, 89]. The spectrum used as experimental reference in Paper I was taken from ref. [88], while the experimental reference spectrum in Paper II was

\(^1\)For an excellent experimental review on XAS from liquid water and ice we refer to a paper with the title “X-ray Absorption Spectroscopy and X-ray Raman Scattering of Water and Ice; An Experimental View” by Nilsson et al. (ref. [89]) to appear in a special issue on water and hydrogen bonds in the Journal of Electron Spectroscopy and Related Phenomena early 2010.
Figure 4.1: \(O-H_1\) Bond length [Å] vs. Intensity.

Figure 4.2: Left: Correlation between uncoordinated \(O-H_1\) internal distance and integrated intensity before the pre-edge for the most asymmetric (a\(_5\),6) model. The straight line corresponds to a least-squares fit of points with intensity greater than 1. Right: XAS spectra computed for the most asymmetric (a\(_5\),6) model with (bottom) and without (top) separate vibrational distributions for the H-bonded and non-H-bonded hydrogens.

that of ref. [6]. They were at the time of writing the papers considered the most appropriate experimental references. In Paper IV the most recent spectrum from the STXM transmission mode experiments from ref. [89] was used. Although the most recent data are the most accurate and reliably reproducible [89], differences with previous measurements are small and the mismatch between the computed and experimental spectra in Figure 4.1 is much larger than the remaining experimental uncertainties. It can thus be ruled out completely that the mismatch in Figure 4.1 could be due mainly to experimental errors.

Also the computed spectra are of course associated with errors. The relevant question here is how large these errors are compared to the mismatch in Figure 4.1 between the computed spectrum and experiment. The in-depth study of the uncertainties associated with TP-DFT spectrum calculations presented in Paper IV (and to some extent already treated in Chapter 2) addresses this issue further. It is sufficient to note here, that the spectrum calculations in Paper I should be accurate enough to reproduce the energy position, width and over-all shape of the spectrum. Although perhaps the sharp pre-edge feature at 535 eV would not come out as sharp in the spectrum calculations as in the experiment even if a representative structure was at hand (due mainly to lack of statistics, an incomplete description of zero-point effects, truncation effects etc.), the intensity ratios between different spectral regions should be fairly reliable; the absolute energy scale in the computed spectra is more reliable than the intensities. What is left then to investigate are the structures.

A correlation was found for the most asymmetric a\(_5\),6 model, between the integrated pre-pre-edge intensity (intensity below 533.5 eV) and the molecular O-H1 distance (Figure 4.2). From Table 4.1 we see that H1 is always the hydrogen atom in the water molecule carrying the lowest charge (or no charge at all) in the EPSR simulation. Therefore, H1 is also the hydrogen atom which is the least likely to form a hydrogen bond. The state corresponding to the pre-edge spectral feature is localized around the broken H-bond. It is anti-bonding with respect to both the H-bond i.e. to the oxygen atoms on the surrounding molecules, as well as to the
covalent O-H bond. An elongation of the O-H distance causes the corresponding anti-bonding state to go down in energy, hence the correlation with enhanced pre-pre-edge intensity. This gives a hint at the importance of the interplay between molecular and H-bonding geometry to understand and describe the details of the XAS spectrum of liquid water and similar systems.

Based on these findings a new EPSR simulation was set up assigning different O-H mean distances for the differently charged H atoms. The resulting XAS spectrum is shown in Figure 4.2. The situation is somewhat improved. Much of the pre-pre-edge intensity seen previously has been shifted to higher energies. However, there is still intensity in the computed spectrum before the true spectrum onset. The origin of the remaining pre-pre-edge intensity can also be found in the structures. A further analysis of the structures still contributing to the pre-pre-edge intensity deemed likely that much of it was due to unphysical H⋯H interactions. The structural asymmetry was imposed by a charge asymmetry in the reference potential. But with no charge on half of the hydrogen atoms there is nothing in the simulation to prevent these atoms to come in close proximity of each other. The diffraction data itself does not set strict enough constraints. Pockets in the structure with H atoms pointing towards each other stabilize the lowest unoccupied states and drag them down in energy to the pre-pre-edge region. This scenario is similar to what is found for the solvated electron [60].

It is concluded in Paper I that the asymmetric structure models investigated are, despite their high number of broken H-bonds, not compatible with XAS.

**IR/Raman Analysis**

Two different approaches were used to model the IR/Raman spectrum of an isolated OH stretch of dilute HOD in D2O for the various structure models from ref. [81]; the one due to Skinner and co-workers [91, 92], relating the E-field to the frequency, and the approach of Mukamel and co-workers [90] where also the E-field gradient is used. Figure 4.3 shows the resulting E-field distribution and spectra from the method of Skinner and co-workers (left) and Mukamel and co-workers (right), for both the symmetric (a2) model (top), and the most asymmetric (a2,6) structure model (bottom). The noisy line (top, left and right) is the resulting curve from an SPC/E MD simulation.

Starting with the symmetric (a2) model (top) we have qualitatively similar spectra using the two different approaches (left and right). Both show one single broad peak, as does also the experiment [93]. Both methods predict a blue-shifted vibrational spectrum for the symmetric (a2) model compared to SPC/E.

Going now to the asymmetric (a2,6) structure model (bottom) a completely different picture arises. While the method of Mukamel and co-workers (right) show a similar spectrum as for the (a2) model, the method of Skinner and co-workers (left) give a bimodal E-field distribution far from the symmetric (a2) model. The two different approaches to estimate the IR/Raman spectrum thus give similar results for the symmetric (a2) model but differ widely in their predictions of the IR/Raman spectrum for the most asymmetric (a2,6) structure model.

The IR/Raman study in Paper I is rather inconclusive, since the two different commonly used approximations to compute the vibrational spectrum give similar
results for the most symmetric structure model, while they differ significantly in their predictions of the spectral shape for the most asymmetric structure model. However, although the correlation between frequency and E-field in the method of Skinner and co-workers is not a perfect linear relation [94] it is still unlikely that a structure with a bi-modal and highly blue-shifted E-field distribution like that from the (a2,6) model would be compatible with the experimental vibrational spectrum. Indeed, a later more rigorous treatment of the vibrational spectrum of the model showed this clearly [94].

4.1.2 Two Extreme Structure Models of Liquid Water

Two structure models (with 2304 molecules), were created in Paper II using the RMC technique by fitting simultaneously to XD data from ref. [20] and to ND data of five isotopic mixtures of water from ref. [21]. Included in the fit was also the distribution of E-field strengths projected in the direction of each O-H oscillator, as an approximation to the O-H stretch vibrational spectrum of dilute HOD in D2O [91], with the E-field distribution from an MD simulation with the TIP4P-pol2 [95] potential as reference. The distributions of internal molecular geometries (O-H distances and H-O-H angles) were fitted to Gaussian distributions of the same width as obtained from a path-integral MD (PIMD) simulation of the liquid [85]. A series
of geometrical H-bonding cone criteria were also applied to drive the fits into two structural models with highly different H-bond connectivity, one symmetric similar to what would be expected from an MD simulation of the liquid, and one asymmetric similar to what was proposed in ref. [6]. The two structure models were labeled DD and SD, from their respective high fractions of molecules in double-donor (DD), and single-donor (SD) local H-bond configurations. The DD structure model has 81% DD and 18% SD molecules, while the SD structure model has 21% DD and 74% SD molecules.

A large part of the work with Paper II was devoted to the implementation of these geometrical constraints for H-bonding in the RMC++ code [83]. Details of the implementation was given in the supplementary online material [96], and has also been discussed in Chapter 3 of this thesis.

![Figure 4.4: Resulting fits to diffraction data from simultaneous RMC fits to XD and ND data as well as E-field distribution, using the DD model (left) and the SD model (right). The diffraction data sets are (a) XD [20] and (b-f) ND from ref. [21] for five different mixtures of D$_2$O and H$_2$O: (b) 100% D$_2$O, (c) 75% D$_2$O and 25% H$_2$O, (d) 50% D$_2$O and 50% H$_2$O, (e) 25% D$_2$O and 75% H$_2$O, (f) 100% H$_2$O](image)

**Diffraction Analysis**

The fit to diffraction data was equally good for both models (Figure 4.4). That the H-bond constraints actually succeeded in creating two differently H-bonded structure models is clearly seen in Figure 4.5, where the distribution of H-bond angles, as well as the asymmetry of H-bond angles and H-bond distances are plotted, together with corresponding distributions from a TIP4P-pol2 MD simulation. The DD model is similar to the MD model but has somewhat wider distributions. The SD model on the other hand has a bi-modal distribution, a clear indication that the two structure models indeed have qualitatively different H-bond topologies. The mere existence of these two structure models disproves the often expressed belief that diffraction data would be in support only of a tetrahedrally connected liquid.
Claims have been made in the literature that the TIP4P-pol2 MD potential model generates structures in almost perfect agreement with XD experiments [19]. It was somehow forgotten, however, that already at the time when the popular SPC/E potential was introduced, which gives pair-correlation functions in rather close resemblance with TIP4P-pol2, the resulting O-O PCF did not fit diffraction more than on a qualitative level [17]. A closer look at the computed XD signals from these models can tell us why.

The left panel in Figure 4.6 shows a comparison of the O-O PCFs from the TIP4P-pol2 and SPC/E MD potentials at room temperature, with corresponding PCFs from the RMC-DD structure model and the EPSR simulations from ref. [21] against two different XD data sets. The two MD models have a sharp first peak in their O-O PCFs while the first minimum gets deeper than the PCFs fitting diffraction data. The SPC/E curve is below the one from TIP4P-pol2 in this region, which has importance in Q-space.

The right panel in Figure 4.6 shows the MD models and the RMC model in Q-space, in comparison with the experimental XD data from ref. [20]. There is a mismatch in phase at higher Q between the MD models on the one hand and the experiment and the RMC-DD model on the other. This is indicative of a too short first O-O distance in the MD models. There is furthermore a mismatch in the intensity ratio of the first two peaks for SPC/E compared to the experiment. This intensity ratio is related to the first dip in the PCF and the trend is similar for variation with temperature [97]. In that sense the SPC/E structure can be regarded in terms of its O-O PCF as qualitatively corresponding to data at a lower temperature; thus a clear indication of over-structuring.

Figure 4.5: Distributions of geometrical parameters characterizing local geometries for three different structures, the SD and DD RMC models and a TIP4P-pol2 [95] MD model. Distribution of H-bond angles (left), distribution of H-bond angle and H-bond distance differences between the two donating H-bonds on each molecule (middle) and (right).

**IR/Raman Analysis**

The E-field distribution from an MD simulation is of course not an experimental set of data, and although there is indeed a correlation between vibrational frequency and projected E-field this correlation is associated with quite large uncertainties (see ref. [94] and references therein). Therefore, larger deviations from the reference were
4.1. PAPERS I, II AND III

Figure 4.6: Left: O-O pair correlation functions derived from the RMC fitted DD model and EPSR generated models [21] fitted to neutron diffraction data together with either the Hura et al. [20] or the Narten and Levy [22] x-ray diffraction data sets. In the figure is also shown a comparison with structural models obtained from MD simulations using the SPC/E [17] and the TIP4P-pol2 [95] force fields. Right: Comparison of $S(Q)$ for MD simulations using the SPC/E and TIP4P-pol2 force fields and the RMC-DD model with the $S(Q)$ derived from the experimental data of Hura et al.. The bars represent the peak positions for each oscillation in the experimentally derived and MD obtained $S(Q)$.

allowed in the fit to the E-field compared to the fit to the diffraction data. Never the less, the fit to the E-field (Figure 4.7) is quite satisfactory, and similar for both structure models.

The right panel in Figure 4.7 shows the E-field distributions from the two structure models, split up into contributions from water molecules in different H-bond configurations, as determined according to the geometrical cone definition of ref. [6]. Contrary to what one would expect, the same type of O-H oscillator in the two different structure models spans different regions of the E-field distribution.

Recent pump-probe experiments on water [98] if interpreted in terms of the SD model, would not necessarily lead to the conclusion that the dynamics of the H-bonding network is ultra-fast [99, 100]. Instead the fast observed spectral shift could be due to a non-H-bonding OH oscillator on a highly librationally excited water molecule in SD configuration changing place with the H-bonded OH on the same molecule without affecting the H-bonding network.

In a follow-up study to Paper II, Ljungberg et al. [94] did a careful analysis of the E-field approximation to the vibrational spectrum. They confirmed that there is indeed a correlation between projected E-field and vibrational frequency, however the mapping is not linear and was furthermore shown to be model dependent, i.e. to reliably model the vibrational spectrum with the E-field approximation this mapping must be determined beforehand for each case.
CHAPTER 4. SUMMARY OF MAIN RESULTS

4.1.3 Different Levels of Tetrahedrality

The XAS study of Wernet et al. [6] proposed an asymmetric local structure of liquid water as defined by a geometrical H-bonding criterion involving the position of the hydrogens. The subsequent analysis of the differently H-bonded structure models of the liquid presented above was focusing on H-bonding according to the same geometrical H-bond criterion. A tetrahedral local structure was defined as a central water molecule having four H-bonds according to this geometrical H-bond criterion. But this definition of H-bonding says little about the tetrahedrality of the oxygen sub-lattice. It is in principle possible to have a structure with four H-bonds per water molecule according to the cone definition, but which has its oxygen sub-lattice quite distorted from the perfectly tetrahedral sub-lattice of ice. It is in the same way possible that a structure which is asymmetrically H-bonded according to the cone definition has an oxygen sub-lattice with a high level of tetrahedrality. The latter turns out to be the case for the SD structure model in Paper II. The origin of the tetrahedrality of the oxygen sub-lattice in the SD model can, as will be discussed below, be traced to the inclusion of the E-field in the RMC fitting.

The tetrahedrality of the oxygen sub-lattice can be characterized by the distribution of O-O-O angles within a certain cutoff from the central water molecule, corresponding to the first coordination shell. A unimodal distribution of O-O-O angles centered around the tetrahedral angle 109.5° would be expected from a tetra-

Figure 4.7: Left: Resulting E-field distribution from the simultaneous RMC fits to x-ray and neutron diffraction data as well as E-field distribution using the (a) DD and (c) asymmetric models. The reference distribution (b) is taken from a TIP4P-pol2 simulation [95]. Right: Decomposition of the E-field distribution into contributions from O-H groups in doubly H-bonded (DD) species, H-bonded O-H in asymmetric SD species (SD-B) and non-H-bonded OH in asymmetric species (SD-N). Non-donor (ND) contributions are small in the DD model and negligible in the asymmetrical SD model. (a) Symmetric DD model, (b) asymmetric SD model.
4.1. PAPERS I, II AND III

Figure 4.8: Left: Distribution of O-O-O angles (normalized to $\sin(\theta_{OOO})$ and using a 3.4 Å cutoff), for the SD and DD models of Paper II, together with the FREE and SYM models of Paper III. Right: The O-O-O distributions for all models of Paper III, together with the SCP/E [17] and TIP4P-pol2 [95] MD models.

The $\langle q \rangle$ parameter [101, 102] defined as

$$\langle q \rangle = 1 - \left\langle \left( \cos \theta_{OOO} + \frac{1}{3} \right)^2 \right\rangle$$

(4.1)

where $\theta_{OOO}$ is the angle between a central oxygen and two of its nearest neighboring oxygen atoms, and the angular brackets denotes averaging over all such angles in the investigated structure model, can further be used to reduce the O-O-O angle...
distribution to a single number. \( \langle q \rangle \) equals one for a perfect tetrahedral structure like ice Ih, and is smaller for less tetrahedral structures. It is however highly important to have relevant references for the \( \langle q \rangle \) scale when comparing different structure models. The random structure of water molecules with the correct density, as represented by a hard sphere Monte-Carlo (HSMC) simulation of water gives a \( \langle q \rangle \) value of 0.470, while the SPC/E MD potential which gives a structure in accordance with the standard model of liquid water as a distorted tetrahedral network gets the \( \langle q \rangle \) value of 0.576.

In Paper III, four new structure models (with 18432 molecules), labeled FREE, ASYM, SYM and MIX, were generated using the same RMC framework as in Paper II, but without fitting the E-field to give a more unbiased fit to the diffraction data. The resulting structures were all in very good agreement with XD and ND data. The FREE model had no H-bond constraints thus representing the most disordered structure still compatible with the diffraction data. The ASYM and SYM models were setup to maximize the number of asymmetrically and symmetrically H-bonded molecules respectively. The MIX model has constraints for both very asymmetrically and symmetrically H-bonded molecules representing a crude two-state model of the liquid. A HSMC simulation with the same parameters as the FREE model, but without fitting the diffraction data, was used as reference system.

The distribution of O-O-O angles for the SD and DD structure models from Paper II are shown in the left panel in Figure 4.8 together with the FREE and SYM models from Paper III. Despite the noisy statistics due to the smaller number of molecules in the SD and DD structures there is no doubt that in terms of O-O-O angles, the DD and the SD model are both more tetrahedral than the SYM model. The right panel shows the distribution of O-O-O angles for all models of Paper III, as well as for the SPC/E [17] and TIP4P-pol2 [95] MD models. The \( \langle q \rangle \) values for all models are presented in Table 4.2.

Table 4.2: Value of the \( \langle q \rangle \) parameter and average number of H-bonds per molecule for the different structure models, using a first shell cutoff of 3.4 Å. The first row gives the \( \langle q \rangle \) value for each model; the second row gives the \( \langle q \rangle \) values on a relative scale, where HSMC represents 0 and SPC/E represents 100; the third row gives the average number of H-bonds per water molecule according to the cone criterion of ref. [6].

<table>
<thead>
<tr>
<th></th>
<th>SD</th>
<th>DD</th>
<th>FREE</th>
<th>ASYM</th>
<th>SYM</th>
<th>MIX</th>
<th>SPC/E</th>
<th>TIP4P-pol2</th>
<th>HSMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \langle q \rangle )</td>
<td>0.592</td>
<td>0.603</td>
<td>0.499</td>
<td>0.488</td>
<td>0.552</td>
<td>0.489</td>
<td>0.576</td>
<td>0.586</td>
<td>0.470</td>
</tr>
<tr>
<td>rel. ( q )</td>
<td>115.1</td>
<td>125.5</td>
<td>27.4</td>
<td>17.0</td>
<td>77.4</td>
<td>17.9</td>
<td>100.0</td>
<td>116.0</td>
<td>0</td>
</tr>
<tr>
<td>av. HB</td>
<td>2.35</td>
<td>3.41</td>
<td>2.28</td>
<td>2.08</td>
<td>3.38</td>
<td>2.62</td>
<td>3.22</td>
<td>3.12</td>
<td>1.16</td>
</tr>
</tbody>
</table>

Based on Figure 4.8 and Table 4.2 some interesting insights can be made. Firstly, it seems like the E-field included as a reference in the SD and DD models gave rise to structures with a tetrahedral oxygen sub-lattice despite the imposed H-bonding constraints (see Table 4.2). The SYM and ASYM models which have very similar H-bonding constraints as the DD and SD models, respectively, but were not fitted to the E-field, have quite different oxygen sub-lattice tetrahedrality. Secondly, there are two major classes of models based on the O-O-O tetrahedrality. The FREE, ASYM
and MIX models all have similar $\theta_{OOO}$ distributions with low O-O-O tetrahedrality and a sharp peak at around 60° corresponding to waters at interstitial positions in the first coordination shell, while the SYM, DD, SD and the two MD models fall into another class with high O-O-O tetrahedrality. It thus seems like tetrahedrality in the

![Figure SMXY](image_url)

The O-O, O-H and H-H PCFs from the FREE, SYM, MIX and ASYM RMC models, together with the corresponding curves for the SPC/E [17] and TIP4P-pol2 [95] MD models at room temperature.

Figure 4.9: The O-O, O-H and H-H PCFs from the FREE, SYM, MIX and ASYM RMC models, together with the corresponding curves for the SPC/E [17] and TIP4P-pol2 [95] MD models at room temperature.
Figure 4.10: Left: Partial structure factors $A(Q)$ for the FREE model and the SPC/E [17] and TIP4P-pol2 [95] MD models. Right: The partial structure factors for the two MD models combined into neutron structure factors of different mixtures of $H_2O$ and $D_2O$ together with experimental curves from ref. [21]. From the top: 100% $D_2O$, 75% $D_2O$ and 25% $H_2O$, 50% $D_2O$ and 50% $H_2O$, 25% $D_2O$ and 75% $H_2O$, 100% $H_2O$. Intramolecular contributions are indicated.

oxygen sub-lattice does not show up in the models unless imposed by tetrahedral H-bond constraints (SYM, DD), the inclusion of the E-field based on an MD simulation as reference in the RMC simulations (SD, DD), or from the direct working of an MD potential (TIP4P-pol2, SPC/E). Tetrahedrality is thus not well defined by diffraction data, neither in terms of H-bond topology nor in terms of O-O correlations.

Despite these perhaps discouraging results it should not be forgotten that diffraction data holds valuable information on the PCFs. Especially for cases such as water where it is possible by isotopic substitution to obtain information on all partials. XD and ND data can furthermore be accurately modeled using the equations in Chapter 3. It is therefore reasonable to demand from a structure model of liquid water from which the local configurations are of interest, that it should reproduce the diffraction pattern.

4.1.4 Diffraction on Water in Detail

As discussed in Chapter 3 the total structure factor $S(Q)$ is a weighted sum of the partial structure factors $A(Q)$ connected to the PCFs via the FT relation eqn. 3.8. Diffraction is thus sensitive to the spherically averaged distribution of distances in the liquid. Figure 4.9 shows the PCFs for the four structure models from Paper
III together with PCFs resulting from simulations with the SPC/E and TIP4P-pol2 MD potential models. We have already seen in Section 4.1.2 above, that the SPC/E and the TIP4P-pol2 MD potentials give over-structured O-O PCFs. This is again reproduced in Figure 4.9. While XD is particularly sensitive to the O-O PCF, ND sees more of the O-H and H-H PCFs due to the fortunate fact that hydrogen and deuterium have widely different neutron scattering lengths. Using different isotopic mixtures of water thus makes it possible to extract a full set of PCFs. Figure 4.9 also shows the O-H and H-H PCFs. The MD models have, for all PCFs, too sharp peaks and too deep minima compared to the RMC models.

We can look in even more detail, and investigate the MD models directly in Q-space where the diffraction measurements have been made. It is always desirable to make the fit, or comparison, directly in Q-space. The diffraction data are inevitably measured over a finite Q-interval. Taking a Q to r transform using a small interval in Q-space gives rise to Fourier artifacts and numerical instability. Taking instead the r to Q transform using PCFs from an MD simulation makes it possible to systematically reduce the numerical uncertainties related to the Fourier transform simply by using a larger simulation box.

Figure 4.10 (left) shows the partial structure factors, A(Q), for the two investigated MD models (obtained from the PCFs via eqn. 3.8). Since there are no true experimental A(Q) a comparison is made against the experimentally derived A(Q) extracted from the RMC-FREE model, which makes a good fit to both XD and ND data. These experimentally derived A(Q)s are the best approximations we have to their experimental counterparts. Also, to get an as fair comparison as possible for the MD models the intramolecular contribution to the scattering in the O-H and H-H partials was here replaced with the corresponding intramolecular signal from the RMC-FREE model. This gives a significant improvement of the fit with experiment for the MD models. The right panel shows the A(Q)s summed together via eqn. 3.9 to correspond to the ND pattern of five different mixtures of H2O and D2O. The reference curves here are the experimental data from ref. [21].

The intramolecular contribution to the diffraction signal is also indicated in Figure 4.10 (right). It is clear that the intramolecular scattering completely dominates the signal for Q-values of around 7 Å⁻¹ and above. This inevitably makes neutron diffraction a rather blunt probe of the details of the PCFs. Going back to Figure 4.9 we see that even though the RMC models all agree equally well with the ND data they show quite some variation particularly in the important first “H-bonding” peak in the O-H PCF. These differences cannot be resolved by the presently available neutron data. The MD models on the other hand do not fall within the limits of the resolution. In particular, the too short first O-H distance manifests itself in a small but important mismatch with the ND data mainly in the region around 5 Å⁻¹.
4.2 Paper IV

Paper IV makes a contribution to the theoretical description of XAS by an in-depth investigation of some important technical aspects of the TP-DFT spectrum calculations\(^2\). The reliability of conclusions regarding an experimental system which are based on theoretical calculations will of course be dependent on the reliability of the calculations themselves. Paper IV represents an attempt to assess the error bars associated with XAS computed within the TP-DFT approximation. How reliably can a spectrum be reproduced for a given geometry using this method?

Just as it is of fundamental importance to keep developing and refining the theoretical description of XAS, it is necessary to determine what we can and what we cannot say about XAS on water from the TP-DFT calculations. We will begin the discussion with the XAS spectrum of a gas phase water molecule for which the geometry, as well as its ground state vibrational wave function is well known. From there we move over to condensed phase water in the form of ice Ih.

When aiming for a reliable experimental model system it came to our knowledge that there are severe experimental difficulties in preparing good quality ice samples for XAS measurements. The experimental ice spectra differ a lot with different preparation and measuring techniques (see Figure 4.15). Recent development on the experimental side makes likely that spectra previously reported as ice Ih [6, 63, 103], are indeed spectra from different mixtures of cubic ice (Ic) and high density amorphous ice (HDA) [104, 89]. This is of course highly unsatisfactory from a theoretical point of view where access to a reliable test system is a crucial component in assessing the reliability of the calculations; but not enough reason not to carry out an investigation. The best we can do is to make as careful calculations as possible and compare with different theoretical descriptions. Once the experimental development has reached the point where a reliable ice Ih spectrum can be measured our calculation will have their experimental reference.

4.2.1 The Importance of Sampling Structures

The XAS spectrum of gas phase water is experimentally well established [63, 105]. The experimental spectrum (Figure 4.11 dashed line) shows three well separated peaks, the strongly vibrationally broadened anti-bonding 4a\(_1\) and 2b\(_2\) states, and the sharper non-bonding Rydberg 2b\(_1\) state. The series of Rydberg states then converges into the continuum at the 1s ionisation potential at 539.8 eV [106]. Figure 4.11 (a) shows the properly energy calibrated computed spectrum (as described in Section 2.3.2) of a single gas phase water molecule in its experimental equilibrium geometry, treated with a flat Gaussian broadening of 0.2 eV full width at half maximum (FWHM) corresponding roughly to the life time of the oxygen 1s core-hole [60]. A very large augmentation basis (\(~3500\) functions) was used to obtain a reliable description of the continuum part of the spectrum. The energy positions of the peaks turn out quite well. The 4a\(_1\) and 2b\(_2\) peaks come out 0.2 eV too high in energy, while the energy position of the Rydberg 2b\(_1\) state is 0.45 eV too high.

\(^2\)The augmentation basis-set, applied broadening and functional dependence of the TP-DFT XAS calculations presented in Paper IV have been discussed already in Chapter 2 of this thesis and will not be commented on further.
4.2. PAPER IV

Figure 4.11: Gas phase XAS for water: experiment (dashed line) from ref.[63]. (a) A single computed spectrum with the molecule at the equilibrium geometry broadened 0.2 eV. (b) Sum of 8000 computed spectra with the molecule at different geometries according to the zero-point vibrational distribution, each contributing spectrum ΔKS shifted and CEBE corrected and broadened 0.2 eV. (c) The 8000 spectra all ΔKS shifted with the same reference ground state energy to account for the excitation occurring from the ground state zero-point energy level, with an applied over-all shift to coincide in energy position with the 4a₁ peak.

Since we have only broadened the spectrum with the life time broadening and not taken into account any vibrational effects the widths of the two first peaks are not well reproduced.

For a simple system like a gas phase water molecule it is possible to accurately obtain potential energy surfaces for the ground and excited states and rigorously treat all vibrational effects in the spectrum [107]. Another much simpler approach would be to account for the vibrational effects qualitatively by using a different Gaussian broadening for each of the three first states [108], although such an approach would be purely cosmetic and would not contribute much to our understanding of the underlying physical phenomena governing the broadening. Yet another approach is possible however. For dissociative excited states, such as the 4a₁ state of the gas phase water molecule [109], where there are no discrete vibrational levels, the Franck-Condon profile becomes dependent only on the square of the ground state vibrational wave function, i.e. on the vibrational probability distribution in the ground state. The shape of the resulting spectrum can then be pictured as the result of a reflection of the geometry distribution in “position space”, via the electronic excited state energy curve, to a broadened spectrum in “energy space” [110]. The shape of the excited state curve will govern the asymmetry of the observed broadened spectral peaks.
We can in analogy with the above picture view the reflection (or projection) of
the ground state vibrational distribution as the result of the sum of a large number
of spectra taken at different geometries which together sum up to the ground-state
vibrational distribution. The zero-point distribution of e.g. O-H distances in a water
molecule does not represent a smeared out proton, but the probability of finding
the proton at a certain distance from the oxygen in the event of a position measure-
ment. The XAS process thus works as a position measurement in the sense that
the incoming photon will interact with a water molecule only if the molecular geo-
metry is found in a position where the excitation energy equals the photon energy.
If the molecule is found in a different geometry, for which the photon is not reso-
nant, interaction does not occur. X-ray photons of a certain energy thus selectively
excite water molecules in a particular geometry. Summing individual spectrum con-
tributions taken at a set of geometries representative of the zero-point vibrational
distribution should leave us with a spectrum reproducing the vibrational broadening
of the dissociative states.

Figure 4.11 (b) shows the sum of 8000 spectra computed from geometries sampled
from the zero-point vibrational distribution as determined by solving the vibrational
problem on the electronic ground state potential energy surface [111]. Each spectrum
contributing to the sum is energy calibrated and broadened as in Figure 4.11 (a) only
with Gaussians of 0.2 eV FWHM, yet the full Franck-Condon profile is captured.
The widths of the 4a1 and 2b2 states are much broader than for the Rydberg 2b1 state,
in good qualitative agreement with the experiment. The spectrum is normalized to
coincide with the experiment in the height of the 4a1 peak. That the width of the
4a1 peak is somewhat overestimated from the calculations can largely be explained
by the zero-point vibrational energy.

When obtaining the energy scale from the standard ΔKS+CEBE procedure (Sec-
tion 2.3.2 above), the computed ground state energy will follow the ground state
potential energy surface for different geometries. However, if the zero-point energy
is correctly accounted for the ground state energy must be the same for all geo-
metries. Modifying the ΔKS shifting procedure so that we for each geometry calculate
the first excited state energy, but use the same reference ground state energy for
all geometries, produces a shape of the 4a1 peak in much better agreement with
experiment. It should be noted here that since the reference ground state energy
used for all geometries was arbitrarily chosen the final summed spectrum had to be shifted in energy to coincide with the experiment. The result is shown in Figure 4.11 (c). A marked improvement is noted for the shape of the 4a₁ state although this happens at the expense of the 2b₂ and 2b₁ peaks getting smeared out and shifted up in energy.

Similar effects of sampling the vibrational distributions can be observed for a condensed phase system. The centroid of a PIMD simulation corresponds roughly to the energy minimized structure. Taking instead the geometry from one bead of the simulation gives a structure with zero-point vibrational disorder. In Figure 4.12 the computed centroid spectrum, summed from nearly all local structures of a 1523 molecules PIMD SPC/E ice Ih simulation at 100K, is compared with the corresponding spectrum computed from one of the beads. Large spectral changes occur when going from a centroid to a bead structure. Particularly the post-edge resonance at $\sim 540$ eV is smeared out and shifted to lower energies. The observed trend is expected when loosening up a H-bonded network, however the magnitude of the change is surprisingly large, giving a strong indication of the importance of a correct sampling of the distribution of local geometries already for a relatively well ordered system such as ice Ih at 100K.

### 4.2.2 Different Core-Hole Occupation

As pointed out in Chapter 2 the half core-hole (HCH) approximation has a theoretical justification as an approximation to the Slater transition state approach, however, other core-hole occupations must sometimes be considered for pragmatic reasons. The HCH approximation represents a fair balance between initial and final state effects but for systems with spectra dominated by large excitonic character, such as e.g. the case of fullerenes [112], final state effects needs to be enhanced and the HCH approximation has to be abandoned for the full core-hole (FCH) approximation. In FCH calculations a fully removed electron from the core-level serves as a potential when determining the spectrum.

Cavalleri et al. [108] made an investigation concluding that the HCH approximation is superior to FCH for water and ice. Another study drawing similar conclusions...
was made by Iannuzzi [113]. Common for these two works was the approach of studying the ice spectrum, and not the spectrum of water, as a reference case. Such an approach is indeed quite reasonable, since the structure of ice Ih, in contrary to that of liquid water, is rather well established.

If the structure of water instead is assumed to be close to what comes out from an MD or CPMD simulation, then it is possible, if one also allows for an arbitrary energy shift, to get a seemingly better agreement with experiment for water using the FCH approximation [114]. There are however problems with this reasoning. There should be no difference in the treatment of liquid water and ice, however the FCH approximation gives a very poor description of the ice spectrum [108, 113, 114], as will also be obvious below. An extensive investigation of the different core-hole approximations for XAS calculations of ice Ih was carried out in Paper IV. The resulting spectra in Figure 4.13 (a) shows unambiguously that the FCH approximation works poorly for the case of ice Ih.

In the XCH (for excited core-hole) approximation [115], which is advocated for water and ice by Prendegast and co-workers [116], the first core-excited state is variationally determined and the full spectrum is obtained using the resulting potential. There can be technical reasons for adopting such an approach, e.g. because of problems handling charged systems. It is however very hard to find a theoretical justification. The idea would be that a full core-hole with the excited electron present will give more excitonic character to the first excited state, while the remaining states will feel a partially screened core-hole. The procedure is however completely arbitrary [117]. Initial state effects are lacking and the screening introduced for the higher unoccupied orbitals will be dependent on the character of the lowest core-excited state. In practice it turns out that the XCH calculations for ice give results very similar to FCH.

Figure 4.13 (a) shows the sum of spectra from nearly all local structures from a bead of a 1532 water molecules SPC/E PIMD ice Ih at 100K (the same structure as used in figure 4.12 (a)), using the FCH, XCH and HCH approximations. It is from the figure obvious that the HCH approximation is the only one that gets the spectrum even remotely correct. The FCH and XCH spectra have much intensity in the pre- and main-edge regions but too low in energy, and are completely lacking the post-edge resonance characteristic for H-bonding which dominates the experimental ice spectrum. It is worth noticing here that the energy scale is calibrated in these calculations using the same standard procedure as for the HCH calculations, i.e. the ΔKS+CEBE correction. The HCH spectrum gets a good intensity distribution over the whole energy range of interest, much better than the FCH and XCH spectra, but lacks the sharp pre- and main-edge structures seen in the experiment. The lack of these sharp features in the HCH spectrum will be further commented on in Section 4.2.3 below.

Having seen the dramatic effect on the computed spectrum when shifting from a half to a full core-hole, it can be of interest to connect the two approximations and look closer at the trends when going from one to the other. Figure 4.13 (b) shows spectra from the same ice structure, now computed with core-holes spanning the whole range from FCH to HCH, with step of 0.1 electron. When decreasing the core-hole occupation the post-edge is dragged down in energy in combination with a rapid loss of intensity. Sharp pre- and main-edge structures simultaneously appears, rise in intensity and drift to lower energies.
4.2.3 Cluster vs. Periodic Calculations and Experiments

Figure 4.14 shows the sum of spectra from 174 local structures from one bead of a PIMD simulation of SPC/E D$_2$O ice, with a unit-cell of 192 waters, at 100K. The spectra are obtained using both StoBe [30], with 39 water molecules per cluster, and using the implementation of the TP-DFT spectrum calculations in the periodic real space grid DFT code GPAW [31], where the whole unit cell was used together with $2 \times 2 \times 2$ k-points. Both spectra are treated with a flat 0.5 eV FWHM Gaussian broadening. There is an uncertainty in the absolute energy scale of the GPAW calculations which made it necessary to shift the final summed GPAW spectrum to coincide in energy with the StoBe spectrum. However, the relative energy scale, between different spectra in the total sum, should be well described using both codes. It is striking how similar the spectra look using the different codes to calculate them. It is from this possible to conclude with some confidence that a cluster size of 39 water molecules is enough to well describe the near-edge spectrum of ice, at least when a summed spectrum is considered. The sharp pre- and main-edge features of the experimental spectrum are however not reproduced by neither the cluster nor the periodic calculations.

Experimentally the intensity in the pre- and main-edge regions in the ice spectrum shows sensitivity to different sample preparations and detection techniques. As mentioned above, it is not unlikely that the ice structures thought to be ice Ih, could rather be mixtures of ice Ic and HDA [89]. The near-edge spectra should be nearly identical for ice Ic and Ih, since the two phases only differ in the second coordination shell and beyond. The HDA spectrum has on the other hand been reported as similar to that of liquid water, with strong pre- and main-edge features [119]. It is possible that the SPC/E PIMD ice structure from which computed spectra were taken is not representative of the structure in the experiment. However it could also be that the HCH calculations fail in producing the sharp features of more excitonic
character close to the spectrum onset.

The situation is not satisfactory. What is needed, since the experimental situation is not well determined enough for a quantitative calibration of fine details in the spectrum, is further theoretical work. To test this rigorously a comparison must be made against calculations on a higher level of theory. Unfortunately such investigations fall outside the scope of this thesis.

If we went higher in energy in Figure 4.14 the basis set description in the cluster calculations would soon start to fail. The discussion around the basis set description for a gas phase molecule in Section 2.3.4 is applicable also here. A good description of the spectrum using the Stobe code is therefore limited up to about 15 eV above the edge. With the periodic GPAW calculations however there is nothing to stop us from going much higher in energy. Figure 4.15 shows the GPAW spectrum together with two different experimental spectra. The topmost experimental spectrum taken from ref. [103] was obtained using bulk sensitive secondary electron yield (SEY) detection and measured from an ice film grown on a Pt(111) substrate, while the bottom experimental spectrum was obtained using the both bulk and surface sensitive total electron yield (TEY) detection mode from an ice film at 165 K on a Cu(111) substrate [118]. Here is an illustrative example of the variability of the ice spectrum with preparation and detection mode. What we note is that the pre- and main-edge features are much higher in intensity in the more surface sensitive TEY spectrum.

The TEY spectrum goes high enough in energy to compare with the GPAW calculation all the way up to 565 eV. The experimental spectrum shows some structure in the energy region intermediate between the near-edge spectrum and the onset of the EXAFS oscillations, which has been shown to hold structural information on an intermediate length scale [66]. These spectral features are indicated with vertical lines in the figure; the computed spectrum reproduces them all quite well.

Figure 4.15: Comparison of spectrum of one bead from a PIMD simulation of ice Ih computed with full periodicity using GPAW and experimental spectra from two preparations of a supported ice film using either more bulk-sensitive SEY (top) detection [103] or TEY (bottom) [118].
4.2. **PAPER IV**

Figure 4.16: (thin black line): Sum of 22 spectra randomly chosen according to their H-bond situation as determined by the cone criterion of ref. [6], in either (a) ND, (b) SD and (c) DD configuration, from an RMC structure similar to the MIX model of Paper III. (dotted line): The same spectra but computed with the molecular O-H distances optimized with the TTM2.1-F force-field [120]. (thick grey line): experimental spectrum from ref. [89].

### 4.2.4 H-bond Sensitivity

Although there has for the most part been consensus in the literature regarding the assignment of the spectral features of the XAS spectrum for the condensed phases of water, the magnitude of distortions of the H-bonded network from a perfect ice crystal structure needed for a water-like spectrum to emerge has been subject of debate. In the study of Wernet et al. [6] quite large asymmetric distortions from a perfect tetrahedral local H-bond environment were deemed necessary to obtain a liquid-like spectrum in the calculations. Further theoretical studies (ref. [58] and Papers I and II) showed that applying the cone-criterion of Wernet et al. [6] was not enough to produce a liquid-like spectrum using structures from CPMD, EPSR or RMC simulations. In ref. [58] an even larger asymmetry was suggested. It is however quite unlikely, based on the findings of Paper II and III, that such a structure could possibly be consistent with diffraction.

Figure 4.16 (a)-(c) shows spectra summed from 22 structures of, respectively, non-donor (ND), single-donor (SD) and double-donor (DD) configurations from an RMC structure model using 32 water molecules per cluster and a linearly increasing broadening. The trend is obvious. The spectrum changes with increasing number of H-bonds much in the same way as it changes with increasing core-hole occupation in Figure 4.13, but without the large change in energy position for the spectrum onset. The spectra are somewhat noisy particularly in the pre-edge region mostly because of an insufficient sampling of structures. However the overall shape of the spectra should still be reliable enough to actually say something about the H-bond sensitivity of XAS applied to water.

The double-donor (DD) spectrum (Figure 4.16 (c)) is ice-like with a pronounced post-edge peak. The structures giving rise to this spectrum are quite disordered compared to a perfect ice crystal, although they still have two well defined donating
H-bonds. Loosening up the H-bonding network and breaking half of the H-bonds gives the single-donor (SD) spectrum (Figure 4.16 (b)) which is much more similar to the experiment, with more intensity in the pre- and main-edge regions and less in the post-edge. Note here that the 22 local configurations were picked randomly according to their H-bonding situation. Breaking the remaining H-bond gives the non-donor (ND) spectrum (Figure 4.16 (a)) with a sharp main-edge and an even lower post-edge intensity.

It was shown in Papers I and II (and also in ref. [58]) that a local asymmetry criterion is not enough for a structure model to reproduce XAS. Figure 4.17 shows the computed spectra from the SYM and ASYM models from Paper III. Indeed, both spectra show little resemblance with the experiment. There is too much pre- and pre-pre-edge intensity in both models, and the post-edge resonance is at a position intermediate between the experimental main- and post-edge similar to the a2.6 model of Paper I. It is thus reasonable to assume that these RMC generated structures suffer from many unphysical geometrical situations not excluded by the diffraction data although they are seen in the XAS spectrum as spurious intensity.

In Paper II the SD and DD structure models gave rise to XAS spectra which were very similar and ice-like (Paper II Figure 10). From Table 4.2 we see that the number of H-bonds differ significantly between the SD and DD models while they both show a very high O-O-O tetrahedrality. The ASYM and SYM structure models of Paper III on the other hand show XAS spectra which are highly unphysical, but with a difference spectrum as would be expected from what we saw above on the H-bond sensitivity (Figure 4.16). The difference spectrum in Figure 4.17 is also similar to what one gets experimentally upon heating the liquid and thus breaking H-bonds [6]. From Table 4.2 we see that the ASYM and SYM models differ both in their O-O-O tetrahedrality as well as in their H-bond count. Obviously the H-bond count does not get the whole picture. It is perhaps not too farfetched to propose that also...
the O-O-O tetrahedrality could play a role in predicting the XAS for a structure. Neither is it unlikely that there is some higher-order structural parameter to which XAS is sensitive that would include to some degree both the H-bond count and the O-O-O tetrahedrality, but also go beyond those measures. To find such a correlation however it is necessary to have a well defined systematic way of extracting structural information from large number of computed XAS spectra.

4.3 Papers V and VI

Many more structure models than those which made it into Papers II and III were created using the H-bond constraints in RMC, during the work with this thesis. The aim was to search for structure models in agreement with XAS. It proved extremely hard, however, to obtain any structure model in agreement with XAS, despite having quite sophisticated sets of geometrical constraints with several H-bonding cones.

On the other hand there is certainly a great deal of structural sensitivity in XAS [28]. But since the structural information is convoluted and it is not a straightforward relation in terms of e.g. pair contributions, between local structure and spectrum, and since there are obviously correlations in the structure of importance for XAS which can not be captured with the H-bonding criteria, it would be highly desirable to include the XAS directly into the RMC modeling. This, however, is not practically feasible with the presently available computer resources. Using 46 water molecules per cluster consumes roughly 24 hours of CPU time on a single processor for each individual spectrum calculation. One single attempted move in an RMC simulation would require computing the spectra of 92 local configurations. Even if this could be done in parallel on 92 CPUs it would still take 24 hours per attempted move. Considering the number of moves needed to converge an RMC simulation (on the order of $10^6$ attempted moves), performing an RMC simulation at this speed would take a whole lot more than a life time. Actually, it would take nearly 3000 years.

From the need of analyzing - and the hope of extracting useful structural information from - the already computed XAS spectra, a novel approach for RMC simulations was developed in Paper V, the SpecSwap-RMC method. Although it was particularly aimed at extracting structural information from the already computed XAS spectra of water it was soon realized that the method could open up the possibility of running RMC simulations against any structural probe which can be computed and stored in memory for a large set of local configurations. One would thus not be as limited by the demand for computational efficiency inherent in the normal RMC procedure. The method is described and tested in Paper V, while we in Paper VI use SpecSwap-RMC to model XD and EXAFS of liquid water.

4.3.1 SpecSwap-RMC

The basic idea behind the SpecSwap-RMC method is simple. Take the whole library of already computed spectra and combine a fraction of them into a summed spectrum, which is then compared against an experimental reference. Make a swap-move by trying to replace one of the spectra in the smaller fraction, with one from the library. If the new spectrum gives a better fit the move is accepted, but if the move gave rise to a worsened fit it has an exponentially decaying probability of be-
ing accepted anyway. Keep swapping after the fit has converged and record how often each of the individual spectra appears in the sum. From this information it is possible to construct weights for each spectrum in the library. Since each spectrum is connected with a local structure it is possible to go back and analyze weighted and unweighted distributions of structural parameters as the result of the fit. This procedure can be formalized in a more strict language as follows.

**Formalism**

Define a set $B$ with $N$ elements

$$B \equiv B_N \equiv \{x_N\}$$ (4.2)

We call $B$ the basis-set. Define also a set $S$

$$S_M \subset B_N$$ (4.3)

selected from $B$, with $M \ll N$. This set will be referred to as the sample-set.

Introduce a move operator $\hat{m}$, defined by its action on $S$

$$\hat{m}S_M \equiv S'_M$$ (4.4)

where $S' \subset B$, selected from $B$ by some rule depending on $S$.

Let $S$ represent the state of some system and $P(S)$ some property depending on $S$. Define an error function $\chi^2$, as the squared difference between the property $P(S)$ and a reference property $R$, divided by a parameter $\sigma^2$ related to the assumed uncertainty of the reference.

$$\chi^2 = \frac{(P(S) - R)^2}{\sigma^2}$$ (4.5)

The change in $\chi^2$ due to the application of $\hat{m}$ is then

$$\Delta\chi^2 = \frac{1}{\sigma^2} \left[ (P(\hat{m}S) - R)^2 - (P(S) - R)^2 \right]$$ (4.6)

A Reverse Monte Carlo simulations can now be performed on the system, by successively apply $\hat{m}$ to $S$, and accept or reject the move according to the standard MC acceptance criterion eqns. (3.6) and (3.7). If we let $B$ be the set of all local structures (perhaps a few thousand) in the library, the property $P$ our already computed spectra from the structures and $S$ a smaller fraction (a few hundred) of these structures, we get the SpecSwap-RMC procedure as described in words above.\(^3\)

The results of the SpecSwap-RMC fit will be dependent on the choice and quality of basis-set $B$. To judge the quality and meaning of a fit, it is thus necessary to relate the obtained solution to the basis in a well-defined way. After $\chi^2$ has converged, record how often each element in $B$ appears in $S$. If normalized to the number of

\(^3\)It is described in Paper V how also the standard RMC procedure fits nicely into this generalized formalism.
4.3. PAPERS V AND VI

times $S$ was probed, weights $w_i$ are obtained which converge for each $x_i \in B$. It is then possible to take the weighted sum of each property $P$ from each element $x \in B$

$$P_w = \frac{1}{N} \sum_{i}^{N} w_i P(x_i)$$  \hspace{1cm} (4.7)

and the property without weights

$$P_0 = \frac{1}{N} \sum_{i}^{N} P(x_i)$$  \hspace{1cm} (4.8)

The meaningful comparison, as the result of the SpecSwap-RMC simulation is then to look at how $P_w$ differs from $P_0$.

![Figure 4.18:](image)

(a) SpecSwap-RMC fit to Cu EXAFS reference from ref. [121]. Resulting weighted curve (red) and curve from the basis set (green). (b) Resulting change in $g(r)$, weighted curve (red) and unweighted (green).
Application to EXAFS on Cu

The EXAFS signal from a low temperature Cu crystal has been well characterized using FEFFIT [122]. It therefore makes a perfect first test case of the SpecSwap-RMC method. The basis set was taken as 1000 clusters of Cu atoms randomly displaced from their known perfect lattice positions. The EXAFS signal from the central atom in each cluster was computed with FEFF8.4 [65, 123] using an SCF radius of 4.5 Å and a maximum path-length of 11.2 Å in the scattering path expansion. Each EXAFS calculation takes roughly 30 minutes to compute on a single CPU, thus we have a total CPU time consumption of 500 hours to create the library. The data set used as reference was the Cu data at 50K provided with the IFEFFIT [121] package. 40 structures were used in the sample set and the SpecSwap-RMC simulation was run for $10^8$ attempted moves, with nearly two million accepted moves.

Figure 4.18 (a) shows the experiment (black) together with the signal from the weighted (red) and unweighted (green) basis-set. A large improvement of the fit is seen for the weighted compared to the unweighted basis-set. It is thus obvious that SpecSwap was successful in fitting the reference. The mismatch which still persists between the fitted curve and the reference can be attributed to scattering contributions from higher shells not included in the EXAFS calculations.

If we now go to Figure 4.18 (b) we see a large change in the PCF as a result of the fit. SpecSwap has thus succeeded in extracting structural information from the fit. These results are validated in Figure 4.19 where the first-shell contribution from FEFFIT is compared to that of SpecSwap. The green curve again represents the signal from the unweighted basis-set, while the red curve is the weighted result of the SpecSwap-RMC simulation. The grey curve is the starting point for the FEFFIT fitting procedure and the blue curve is the final outcome of the fit. Although the two different methods, SpecSwap-RMC and FEFFIT, work in fundamentally different ways (SpecSwap-RMC is fitting the whole EXAFS signal in $k$-space while FEFFIT has made a fit to the first-shell contribution in $r$-space) they both arrive at almost identical results.

![Figure 4.19](image.png)
4.3. PAPERS V AND VI

We have here seen a first example on how the SpecSwap-RMC method manages to fit a reference EXAFS curve, and we have seen that the fit resulted in structural changes in terms of the re-weighted PCF in Figure 4.18 (b). We have further confirmed that the method works by comparing first-shell results with FEFFFIT. Now, considering the time it took to compute the EXAFS signal for each basis function, a normal RMC simulation would be impossible to use with the EXAFS calculations at this level of theory. Of course this is not a real problem in the case studied here, since the EXAFS on Cu is already well described using FEFFIT [122]. However, it gives a hint at the new possibilities with the SpecSwap-RMC method. There are many structural probes, e.g. core-level spectroscopies, NMR, or X-ray Compton scattering, which require time consuming quantum-chemistry based calculations to be reliably compared with experiment. These techniques are from now available for RMC modeling.

4.3.2 Diffraction and EXAFS on Water

The O-O PCF of liquid water was determined by fitting XD and ND data in Papers II and III (Figures 4.6 and 4.9). The most recent application of the EPSR procedure to fit diffraction data on water [21] came to similar conclusions regarding the height and position of the first peak in the O-O PCF (Figure 4.6 (left)). We can therefore with some confidence say that the presently available diffraction data on water give a first O-O peak height of 2.3, positioned at about 2.8 Å. A recent x-ray raman based EXAFS study of water and ice Ih [124, 125] using the GNXAS method [126] for the structure analysis, found a much higher first O-O peak (3.5) at a much shorter distance (2.71 Å). Figure 4.20 (left) compares the first peak in the O-O PCF from the GNXAS EXAFS study [124] with an MD simulation using the SPC/E potential [17], with the recent EPSR fit to diffraction data [21], and with the FREE model of Paper III fitted to diffraction data with the RMC technique. We have already seen (Figure 4.6 (right)) that the SPC/E model is over-structured in comparison with the XD data from ref. [20], and that the RMC FREE model gives a near optimal fit. It is therefore quite unlikely that the PCF from GNXAS would be compatible with diffraction. Indeed, when comparing the different O-O PCFs in Q-space (Figure 4.20 (right)) the severe over-structuring of the GNXAS PCF is obvious, with a clear phase shift at higher Q indicating a too short first O-O distance. In Paper VI the SpecSwap-RMC method has been used to cast some light on this discrepancy.

SpecSwap-RMC Fitting of EXAFS

The EXAFS signal was calculated for a set of 7633 local structures taken from the structure models in Papers II and III, as well as from various MD and PIMD simulations with the SPC/E [17], TIP4P-pol2 [95] and TTM2.1-F [120] potentials at different temperatures. The structures, with their associated EXAFS signals, were used in a SpecSwap-RMC fit to the EXAFS signal from ref. [124], with and without simultaneously fitting the O-O PCF from ref. [21] (fitted with EPSR to ND and the Narten XD data [22]). The EXAFS calculations were performed with the FEFF8.4 code [123] using an SCF radius of 4 Å and a maximum path-length of 6 Å in the scattering path expansion, but truncated after 4-legged scattering paths.
**CHAPTER 4. SUMMARY OF MAIN RESULTS**

![Graph 1](image1)

**Figure 4.20:** Left: O-O PCFs from the RMC (the FREE model Paper III) and EPSR [21] fits to diffraction data, compared with the SPC/E and the GNXAS [124] results. Right: corresponding O-O partial structure factors.

![Graph 2](image2)

**Figure 4.21:** Left: resulting EXAFS signals from SpecSwap-RMC fits to EXAFS and EXAFS+PCF, together with the experimental curve from [124] and the unweighted basis set. Right: corresponding O-O PCFs.

The EPSR O-O PCF from ref. [21] was used as target, rather than the one from the RMC FREE model in Paper III, since the low- \( r \) tail of the latter allowed for too many unphysically short O-O distances in the fit. 400 structures were used in the sample set and each SpecSwap-RMC simulation was run for around 10^5 accepted (10^8 attempted) moves.

The \( E_0 \) value, related to the energy position of the edge onset, was fixed before calculating the EXAFS signal from the water structures, by using a bead structure from an SPC/E PIMD simulation of ice Ih at 200 K as a reference system. In ref. [124] EXAFS was measured for both ice Ih and water using the same experimental setup allowing an ice model to be used as reference. The EXAFS signal was calculated from all 1523 local configurations in the simulated ice structure and the sum was compared with the ice experiment. An \( E_0 \) value of -5 eV was found to give the best agreement, with no amplitude re-scaling needed. To ensure the robustness of the calibration, the EXAFS signal from another simulated ice structure (a PIMD simulation of ice using the TIP4P/2005 potential [127]) was also calculated and
compared to experiment. An $E_0$ value of -4 eV was found optimal for this ice reference, which fortunately only had minor effects on the subsequent water fits. An $E_0$ value of -5 eV was therefore consequently used for all calculations on water.

Figure 4.21 shows the EXAFS signals and PCFs from the pure EXAFS fit, and from the fit to EXAFS+PCF, as well as the target EXAFS and PCF and the EXAFS and PCF from the unweighted basis set. We consider first the EXAFS results in the left panel. The pure EXAFS fit is nearly perfect in both amplitude and phase, with a marked improvement compared to the unweighted basis set. The EXAFS curve from fitting both the EXAFS and the O-O PCF lacks amplitude in the first two oscillations but has a correct phase. Considering the uncertainties connected with the $E_0$ calibration and the neglected intramolecular scattering (see discussion in Paper VI) the mismatch in amplitude is not too severe.

Going now to the right panel, the pure EXAFS fit confirms the GNXAS results [124], with a tall first peak in the O-O PCF at a too short distance compared to results from diffraction analysis (Papers II and III and ref. [21]). The peaks seen in the PCF at 3.5 Å and above come from correlations in the basis set and have no significance for the fit to EXAFS. The PCF from the simultaneous fit to EXAFS+PCF, is in good agreement with the target PCF, with only minor differences. We can therefore conclude, that although the GNXAS results in ref. [124] are not compatible with diffraction data, the diffraction data is not incompatible with the EXAFS data, i.e., it is possible to find a structural solution which fits both diffraction and EXAFS. Multiple-scattering contributions have thus compensated for the change in the single-scattering imposed by the fit to the O-O PCF, and left us with a satisfactory fit to the EXAFS curve despite a PCF very different from what is obtained when fitting only to EXAFS.

![Figure 4.22: Distributions of H-bond angles using the basis set weights from the EXAFS fit and the EXAFS+PCF fit, together with the distribution from the unweighted basis set.](image)

Structure Analysis

Since the resulting SpecSwap-RMC fits are expressed in terms of weights for the elements in the basis set, we can make a structural analysis based on weighted and unweighted structural parameters from the underlying structures in the basis set.

We have seen above that there is a clear tendency for the EXAFS data to drive the structure towards a too short first O-O distance, and that the successful simul-
taneous EXAFS+PCF fit was possible because of structural aspects that contribute differently to the EXAFS signal and the O-O PCF. There is a focusing effect in EXAFS for nearly linear configurations involving more than two atoms. For condensed phase water this results in an enhanced amplitude (with a phase shift to lower k) for nearly straight H-bonds. A histogram of the H-bond angles for the pure EXAFS fit, the EXAFS+PCF fit and the unweighted basis set is presented in Figure 4.22. There is indeed a sharpening of the H-bond angles, for both the pure EXAFS fit and the EXAFS+PCF fit. For the pure EXAFS fit this is most likely due to correlations in the basis set, where there is a high probability for a structure with short O-O distances to also have straight H-bonds. This correlation works in the opposite direction for the EXAFS+PCF fit, however, but still the SpecSwap-RMC simulation manages to pick out structures with straight H-bonds. Thus, without the correct inclusion of multiple-scattering contributions in the EXAFS analysis of water a simultaneous fit to EXAFS and diffraction would not be possible.

We can further investigate the structure by looking at weighted and unweighted distributions of the Voronoi polyhedron asphericity parameter $\eta$ defined as

$$\eta_i = \frac{A_i^3}{36\pi V_i^2}$$

where $A_i$ and $V_i$ are the surface area and volume of the Voronoi polyhedron (defined as the part of space which is closer to the central oxygen than to any other oxygen) for the central oxygen atom in the $i$:th basis element. It becomes 1 for a perfect sphere and larger for a more structured Voronoi polyhedron. For instance, a Voronoi polyhedron in an ideal ice crystal gives $\eta = 2.25$. Figure 4.23 shows the weighted and unweighted distributions of asphericity parameters for the pure EXAFS fit (left) and the EXAFS+PCF fit (right), as well as the difference, scaled up to highlight the trends.

There is a clear opposite trend for the two different fits. The pure EXAFS fit becomes more structured compared with the unweighted distribution from the basis set, with a clear enhancement of less spherical, i.e. more structured, local geometries. For the simultaneous fit to EXAFS and the PCF derived from diffraction data, the opposite behavior is noted, with a relative enhancement of less ordered structures.

We have with the study of EXAFS on water in Paper VI seen a first real application of the SpecSwap-RMC procedure. From the structure analysis the conclusions can
be drawn that the focusing effect is important to simultaneously fit both EXAFS and diffraction, giving an enhancement of configurations with straight H-bonds, while the structure from the EXAFS+PCF fit still becomes less well-ordered (see also discussion in Paper VI). We also conclude that the EXAFS data from ref. [124] is compatible with diffraction, although the presented O-O PCF is not.
Chapter 5

Conclusions and Outlook

From our analysis of the diffraction pattern of water we can conclude that a broad range of structure models can be constructed which equally well agree with the data. The diffraction data itself does not require a tetrahedral structure of water, neither in terms of H-bond topology nor in terms of the oxygen sub-lattice tetrahedrality as defined by the distribution of O-O-O angles. But diffraction data still represents an important component in the structure determination of water. The water molecule’s ability to form four directional H-bonds in a near-tetrahedral arrangement is of great importance for the rich polymorphism of solid forms of water, as well as for much of its peculiar behavior as a liquid, but we cannot from diffraction alone determine how large a fraction of the molecules in the liquid are in a near-tetrahedral arrangement. Diffraction data does tell us, however, that liquid water is far from a close-packed system, but has an open network structure with on the average slightly more than four nearest neighbors, and it also gives an experimental determination of the distributions of distances in the liquid; criteria which must be fulfilled by any proposed structure model, regardless of the extent of tetrahedrality. For a more detailed structure determination additional experimental techniques, with qualitatively different structural sensitivity, must be considered.

Based on the computed XAS from our generated structure models, we conclude that, although XAS is indeed sensitive to the local H-bond environment in condensed phase water, a local asymmetry criterion as proposed by Wernet et al. [6] is not enough to reproduce XAS. This conclusion is well within assumed error bars of the spectrum calculations. It is clear that also other correlations matter, although the details have yet to be determined. It is not unlikely that also structural correlations on an intermediate length-scale play an important role for a detailed description of XAS on water. To evaluate a proposed structure model against XAS it is important to realize the very high structural sensitivity in the computed spectra. A realistic description of zero-point motions must be included in the structures to account for the vibrational disorder, and a sufficient sampling of both molecular and H-bond geometries must be performed for a proper account of configurational disorder. For details in the spectrum, correlations between molecular geometry and H-bond geometry will also be of importance.

Technical aspects of the TP-DFT XAS calculations, such as functional, augmentation basis set and core-hole dependent effects have been investigated in this thesis.
Out of the proposed core-hole occupations (HCH, FCH and XCH), the HCH approximation is clearly the most appropriate to describe condensed phase water. The description of continuum states in a localized basis has been compared to periodic calculations for ice Ih with excellent agreement and spectral features at an intermediate energy in the experiment, between 550 and 565 eV, are very well reproduced in the periodic calculations. The post-edge resonance is furthermore well reproduced, but sharp features in the pre- and main-edge regions are lacking for both periodic and cluster calculations. Since the experimental situation is not well determined enough for a quantitative calibration of fine details in the spectrum, further theoretical work is needed to firmly assess the accuracy of the spectrum calculations for condensed phase water.

Finally, to aid in the structure analysis of computationally demanding techniques, such as XAS and EXAFS, the SpecSwap-RMC method was developed. Using a discrete set of local geometries for which all properties of interest have been pre-computed, and expressing the configuration space in the basis of these structures makes it possible to approach the problem of structure determination from core-level spectroscopy in a scheme much alike the conventional RMC method used in diffraction analysis. We can conclude the success of the method by referring to the comparison of modeling EXAFS on Cu metal with the FEFFIT approach and with SpecSwap-RMC yielding nearly identical results. The application to the more challenging case of EXAFS and diffraction on liquid water has indeed cast new light on aspects of the structure. Regardless of the level of theory or the type of data modeled, this tool will be a valuable help in the analysis of data requiring calculations which are too time-consuming to fit into a normal RMC scheme.

The work on diffraction data and H-bond topology presented in this thesis has undoubtedly opened up the range of feasible structure models of liquid water; the standard model as a distorted ice-like tetrahedral network, strongly supported by MD simulations, can no longer be regarded as the only possible model based on diffraction data. New experimental techniques will be available to the application on liquid water in the future, not the least with the development of free-electron lasers operating in the x-ray regime. There will also be theoretical development, aiming at more sophisticated and accurate descriptions of both available and future experimental techniques. At present there is much activity in the field of core-level spectroscopy applied to liquid water, and the near future will have much more to offer. It is important to realize the strengths and limitations of these techniques. Different methods are sensitive to different aspects of the structure and only by combining information from many structural probes can a consistent picture of the liquid be built.

We recently proposed a model of liquid water consistent with x-ray absorption, x-ray emission, diffraction and small angle x-ray scattering (SAXS) in ref. [128]. SAXS was measured on water with high accuracy, yielding direct evidence of density inhomogeneities of a few percent in the liquid at ambient conditions, on a length scale of roughly 1 nm. From the temperature dependence in the SAXS, XAS and XES signals, together with thermodynamical reasoning we arrived at a structure of liquid water as a dynamical equilibrium between tetrahedrally H-bonded, low density structures, in a soup of loosely bound but more densely packed water. Although this may not be the final solution to the structure of liquid water, it is an important
step forward. It is a detailed enough model to actually be tested and it should be fully possible to simulate such a structure with an accurate enough interaction potential and a realistic enough description of the dynamics.

Fundamental progress is seldom possible without a certain level of destruction, and it is always necessary to re-evaluate old truths in the light of new findings. It should be remembered however, that also the new truths become old in the future, as new experimental and theoretical work enter the stage. We thus have to keep being open-minded, critical and creative, work hard and stay firm to our principles. In the end, we add our contributions to the common heap of accumulated knowledge, hope to push development a small step forward, and wait for the judgment of history.
Acknowledgements


Thor och Mathias, jag är stolt och glad över vad vi åstadkommit. Det hade såklart inte varit möjligt utan er inblanding, och jag skulle inte velat gjort det utan er.

Thanks to all other co-authors of the papers: Hirohito Ogasawara, Lars-Åke Näslund, Jan Swenson, Alexander Lyubartsev and Amber Mace, and to all other past and present members of the group.

Sotiris Xantheas, and the people at PNNL. Thank you so much for showing such great hospitality when inviting me to work in your group.

Och ett stort tack till er som genom åren inspirerat mig till fortsatta naturvetenskapliga studier. Tore Brinck, Priidu Pukk, Sven-Åke Frennesson och Börje Sängberg.

Theanne, my times in the US would never have been nearly as good if you weren’t there. I am constantly looking forward to the next time we meet. Matteo, thanks for putting me on the right track. I don’t know how many times I have read your thesis over the years. Klas, du bevisade att det är möjligt. Jag har tänkt på det inte så sällan. Linda, du tänker en liten lykta hopp i mig. Med fler som du vore världen mycket bättre.

Fabbe och Manne, Alex och Adam, Andreas och Viktor, Vänner och Familj; och såklart också Anna, för all kärlek och talamod, Tack!

Mikael Leetmaa
Stockholm 11/11 2009
Sammanfattning

Vatten är ett viktigt ämne. Det är en del av oss, av vår miljö, och är en grundläggande förutsättning för existensen av liv. Men vattnets struktur på molekylär nivå, dvs. hur vattenmolekylerna förhåller sig till varandra geometriskt i vätskan, är fortfarande omtvistat efter mer än 100 år av forskning på området. Den här avhandlingen behandlar teoretiskt vattnets struktur utifrån röntgenabsorptions-spektroskopi (XAS) och röntgen- och neutrondiffraction. Reverse Monte Carlo (RMC) modellering används för att söka efter strukturlösningar på vatten som överensstämmer med flera olika typer av data, med betonning på vikten av en kombination av olika experimentella tekniker för en tillförlitlig strukturbestämning. Geometriska kriterier för vätebindningar har implementerats i RMC för att driva anpassningarna, och på så vis göra det möjligt att utvärdera olika vätebundna strukturmodeller mot datan. Det påvisas att diffракtionsdata på vatten inte ställer några starka specifika krav vad gäller typen av vätebindingstopologi eller distributionen av syre-syre-syre vinklar, samt att klassiska MD simuleringar, med några av de vanligaste interaktionspotentialerna för vatten, ger upphov till O-O och O-H par-korrelationsfunktioner med alltför skarpa första toppar, vid för kort avstånd för att vara i överensstämmelse med diffракtionsdatan. Utifrån en analys av beräknad XAS från genererade strukturmodeller för vatten dras slutsatsen att (i motsats till vad som tidigare föreslagits) ett stort antal brutna vätebindningar i vätskan inte i sig är ett tillräckligt krav på en strukturmodell för att reproduera experimentella XAS data. Ett bidrag till den teoretiska beskrivningen av XAS görs genom en djupgående undersökning av viktiga tekniska aspekter av TP-DFT spektrumberäkningar. Slutligen utvecklas en ny metod för RMC modellering speciellt lämpad för strukturmodellering av beräkningsintensiva storheter, vilket möjliggör strukturmodellering med RMC direkt mot XAS.
Bibliography


[84] Available from: [http://www.isis.rl.ac.uk/RMC/](http://www.isis.rl.ac.uk/RMC/).


[97] L. Fou, S. Breman, and A. Bienenstock. *To Be Published*.


