LIQUID CRYSTAL NMR:
DIRECTOR DYNAMICS AND SMALL SOLUTE MOLECULES

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LIQUID CRYSTAL NMR: DIRECTOR DYNAMICS AND SMALL SOLUTE MOLECULES

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Abstract

The subjects of this thesis are the dynamics of liquid crystals in external electric and magnetic fields as well as the magnetic properties of small molecules, both studied by liquid crystal nuclear magnetic resonance (LC NMR) spectroscopy.

Director dynamics of a liquid crystal 5CB in external magnetic and electric fields was studied by deuterium NMR and spectral simulations. A new theory was developed to explain the peculiar oscillations observed in the experimental spectra collected during fast director rotation. A spectral simulation program based on this new theory was developed and the outcome of the simulations was compared with the experimental results to verify the tenability of the theory.

In the studies on the properties of small solute molecules, LC NMR was utilised to obtain information about anisotropic nuclear magnetic interaction tensors. The nuclear magnetic shielding tensor was studied in methyl halides, the spin-spin coupling tensor in methyl mercury halides and the quadrupolar coupling tensor in deuterated benzenes. The effects of small-amplitude molecular motions and solvent interactions on the obtained parameters were considered in each case. Finally, the experimental results were compared to the corresponding computational NMR parameters calculated in parallel with the experimental work.

Keywords: NMR spectroscopy, liquid crystals, director dynamics in external fields, deuterium NMR, anisotropic nuclear magnetic properties, nuclear magnetic shielding tensor, spin-spin coupling tensor, quadrupolar coupling tensor, dipolar coupling tensor
"Physics is like sex: sure, it may give some practical results, but that's not why we do it."

– Richard Feynman
Acknowledgements

This work has taken place in the NMR research group at the Department of Physics of the University of Oulu. I would like to thank the head of the department, professor Jukka Jokisaari for providing the facilities at my disposal. I would also like to thank the technical staff and the secretariat on the Department for pleasant cooperation.

Professor Jukka Jokisaari has also been my supervisor during the course of this work. I’m indebted to him for sharing his vast knowledge in nuclear magnetic resonance spectroscopy and giving me the opportunity to participate in such an extensive range of projects – some of them outside the scope of this thesis – from the anisotropic properties of small molecules all the way to NMR of biological systems and the magnetic resonance imaging. I’m also grateful to him for providing me with the financial support when needed.

I have also had a chance to visit professor Geoffrey Luckhurst at the University of Southampton in England as well as professor Akihiko Sugimura at the Osaka-Sangyo University in Japan. I’m grateful to both of them for sharing their facilities and making me feel very welcome to their laboratories. Their financial support on my trips is also deeply appreciated. Moreover, I would especially like to thank professor Geoffrey Luckhurst for all the enlightening discussions shedding light on the fascinating world of liquid crystals.

For my theoretical education on NMR spectroscopy I owe to many wonderful courses on NMR, delivered by Docent Juhani Lounila and Professor Jukka Jokisaari. Docent Juhani Lounila is also acknowledged for all the interesting and educational discussions concerning rovibrational motions of the molecules, deformation theory, as well as physics in general.

During the course of this work I have had a privilege to work with many talented people whom have given their invaluable contribution to my work. Professor Juha Vaara is acknowledged, not only for financial support, but especially for pleasant cooperation during our shared projects. Doctor Bakir Timimi is thanked for his friendship and kind guidance which made my work so much easier during my visits to Southampton and Osaka. Professor Jochen Autschbach is acknowledged for his computational work in one of the articles. Docent Petri Ingman, the former facility manager of our NMR laboratory, is gratefully acknowledged for the practical help with the spectrometers. I have had a pleasure to share my knowledge of NMR with many former and present undergraduate and doctoral students of our group and especially I would like to thank Ms. Susanna Ahola, Mr. Sami Järvinen, Dr. Ville-Veikko Telkki, and Dr. Jani Saunavaara for their
contribution in some of the work included in this thesis. I would also like to thank all the other members, past and present, of the NMR research group for creating such a pleasant and friendly working atmosphere; so friendly that some of you have become much more than just workmates. During these years there has also been a varied group of people that has kept me company in the NMR laboratory and during the coffee and lunch breaks and I would like to thank all those persons for our delightful discussions that have covered not only physics, but (mostly) life, the universe and everything.

I would like to thank professors Arnold Maliniak and Carlo Alberto Veracini for reviewing and giving valuable comments on the thesis.

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I am ever grateful for my family for the love, support and encouragement they have given me throughout my whole life. My family and in-laws as well as all my dear friends are also deeply appreciated for reminding me that, even though the life is ruled by physics, you can occasionally forget about it and just enjoy the world as it is. Your impact on my life and thereby on my work is beyond description.

Finally I want to express my deepest gratitude to my loving husband, Perttu, who has encouraged me during the course of this work and helped me through this project, not only by giving his invaluable contribution to the computational work presented in this thesis, but especially by sharing my passion for science and all the joys and griefs of the life beyond physics. I could not imagine my life without you.

Oulu, November 2009

Anu M. Kantola
List of Original Papers

The present thesis consists of an introductory part and the following original papers, which are referred to in the text by their Roman numerals:

I  Kantola AM, Luckhurst GR, Timimi BA, and Sugimura A
   *Deuterium NMR spectroscopy and field-induced director dynamics in liquid crystals.*

II  Kantola AM, Luckhurst GR, Sugimura A, Tanaka T, and Timimi BA
   *Field-induced alignment of the nematic director. Studies of NMR spectral oscillations in the limit of fast director rotation.*
   Manuscript submitted for publication.

III  Kantola AM, Lantto P, Vaara J, and Jokisaari J
    *Carbon and proton shielding tensors in methyl halides.*
    Manuscript submitted for publication.

IV  Autschbach J, Kantola AM, and Jokisaari J
    *NMR measurements and density functional calculations of the $^{199}$Hg–$^{13}$C spin-spin coupling tensors in methyl mercury halides.*

V  Kantola AM, Ahola S, Vaara J, Saunavaara J, and Jokisaari J
    *Experimental and quantum-chemical determination of the $^2$H quadrupole coupling tensor in deuterated benzenes.*
    Physical Chemistry Chemical Physics, 9, 481-490 (2007).

The author of this thesis carried out the experimental work, including the analysis of the data, in Papers I, III and IV, did some of the experiments presented in Papers II and V as
well as performed the analysis of the data in both papers. The author had a major part in
developing the theory of the fast director dynamics in Papers I and II as well as designed
and wrote the MATLAB/Gnu Octave programs and run the spectral simulations for these
papers. The electronic structure calculations on the small molecules were carried out by
Dr. Perttu Lantto from the University of Oulu (Paper III), Prof. Jochen Autschbach from
the State University of New York at Buffalo, USA (Paper IV) and Prof. Juha Vaara from
the University of Oulu (Paper V). All manuscripts were prepared as a team work.

Following papers by the author were excluded as they fall out of the scope of this thesis:

Lantto P, Vaara J, Kantola AM, Telkki V-V, Schimmelphennig B, and Jokisaari J
*Relativistic spin-orbit coupling effects on secondary isotope shifts of $^{13}$C nuclear shielding in CX$_2$ (X =O, S, Se, Te)*

Liimatta E, Kantola AM, and Hassinen IE
*Dual probe fluorescence monitoring of intracellular free calcium during ischemia in mouse heart by using continuous compensation for pH dependence of dissociation constant of Fura-2, and the interference of myoglobin*
Journal of Biochemical and Biophysical Methods, 70, 547-554 (2007).
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>5CB</td>
<td>4-pentyl-4’-cyano-biphenyl (a uniaxial, nematic, thermotropic liquid crystal)</td>
</tr>
<tr>
<td>DQCC</td>
<td>deuterium quadrupole coupling constant</td>
</tr>
<tr>
<td>EFG</td>
<td>electric field gradient</td>
</tr>
<tr>
<td>FID</td>
<td>free induction decay</td>
</tr>
<tr>
<td>LC</td>
<td>liquid crystal</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>PAS</td>
<td>principal axis system</td>
</tr>
<tr>
<td>Phase IV</td>
<td>eutectic mixture of (p)-methoxy-(p’)-(n)-butylazoxybenzenes (a uniaxial, nematic, thermotropic liquid crystal)</td>
</tr>
<tr>
<td>(r_{o}(T))</td>
<td>refers to molecular (r_{o}) geometry (i.e.) an average geometry at temperature (T), including the effects of anharmonic vibrations and centrifugal distortions</td>
</tr>
<tr>
<td>(r_{e})</td>
<td>refers to the molecular equilibrium geometry</td>
</tr>
<tr>
<td>ZLI 1132</td>
<td>eutectic mixture of trans-4-(n)-pentyl-(4’-cyanobiphenyl-4)-cyclohexane and trans-4-(n)-alkyl-(4-cyanophenyl)-cyclohexanes, where alkyl = propyl, pentyl and heptyl (a uniaxial, nematic, thermotropic liquid crystal)</td>
</tr>
<tr>
<td>ZLI 1982</td>
<td>mixture of alkyphenylcyclohexanes, alkylcyclohexanebiphenyls, and bicyclohexanebiphenyls (a uniaxial, nematic, thermotropic liquid crystal)</td>
</tr>
</tbody>
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1 Introduction

1.1 Background

1.1.1 NMR Spectroscopy

The phenomenon of nuclear magnetic resonance (NMR) was experimentally discovered over sixty years ago almost simultaneously by two research groups; Purcell, Torrey and Pound observed the magnetic resonance from a sample of paraffin at Harvard University in December 1945 [1] and, independently from the work by Purcell and his co-workers, Bloch, Hansen and Packard at Stanford University succeeded to obtain an NMR spectrum of water in January 1946 [2]. In 1952 Felix Bloch and Edward Purcell were awarded the Nobel Prize in Physics "for their development of new methods for nuclear magnetic precision measurements and discoveries in connection therewith". Their work was basing on the research of Pauli, Stern, Rabi and other remarkable scientists in the field of quantum mechanics and, specifically, the nuclear spin. In nuclear magnetic resonance, the spin angular momentum of a magnetic nucleus interacts with a magnetic field. This leads to observable resonance frequencies characteristic for each type of nucleus and makes it possible to differentiate, for example, a resonance signal of a hydrogen nucleus, \textit{i.e.} proton, from a resonance signal of a carbon nucleus.

Already in early 1950s it was discovered, that also the nearby electrons and the other nuclei within a molecule affect the energy levels of a nucleus, leading to differences in the NMR spectra for the same type of nuclei, \textit{e.g.} for a proton in an aliphatic chain and a proton in a phenyl ring. This effect of the molecular environment on the NMR spectra is one of the most important features on which the usability of NMR as a versatile research method is built on. However, the beginning of the real success story of NMR spectroscopy culminates to work by Ernst, Jeener and other pioneers of NMR in the 1960s and 70s; the invention of the Fourier Transform NMR (FT-NMR) and the two dimensional spectroscopy expanded the applicability of NMR to totally new dimensions. Richard R. Ernst was rewarded with the Nobel Price in Chemistry 1991 “for his contributions to the development of the methodology of high resolution nuclear magnetic resonance spectroscopy”.

For the general public, the best known application of NMR is probably the magnetic resonance imaging (MRI), nowadays routinely utilised in most modern hospitals. The
invention of the basic idea and the first experiments on MRI also date back to the 1970s, and to acknowledge this ground-breaking work Paul Lauterbur and Sir Peter Mansfield were awarded the Nobel Price in Physiology or Medicine 2003 “for their discoveries concerning magnetic resonance imaging”.

A strong asset of the NMR method is its applicability to gas, liquid and solid state samples, enabling the research to be carried out in the phase that is the most relevant for the system in question. Due to almost hundred percent natural isotopic abundance, high sensitivity and prevalence in natural compounds, proton NMR has turned out to be the choice for most NMR experiments, but dozens of other magnetic nuclei are also regularly utilised in NMR. During the last decades NMR spectroscopy has grown to be one of the leading methods to study a wide range of subjects in physics, chemistry, biochemistry, biology, material sciences, geology and medicine. The increasing importance of NMR in biological research was manifested by the Nobel Price in Chemistry 2002 as it was rewarded to Kurt Wüthrich “for his development of nuclear magnetic resonance spectroscopy for determining the three-dimensional structure of biological macromolecules in solution”.

Developments in the theory and methodology of NMR as well as increasingly efficient computers and higher obtainable magnetic field strengths still give rise to new areas of applications of NMR everyday.

1.1.2 Liquid Crystalline Materials

The history of liquid crystal (LC) materials reaches even further back in time than the history of NMR spectroscopy. The discovery of liquid crystalline materials is traditionally dated to the work of a botanist Friedrich Reinitzer in 1888. These materials share properties of both the liquid state and the solid state as the molecules possess crystal-like order, but they can still move around fairly freely, like molecules in the liquid state. In 1991 Pierre-Gilles de Gennes was awarded the Nobel Price in Physics “for discovering that methods developed for studying order phenomena in simple systems can be generalised to more complex forms of matter, in particular to liquid crystals and polymers”.

Today liquid crystals are found everywhere around us as they are widely used in the display technology in portable computers, mobile phones, LCD-TVs and other devices. These applications are based on the fact that the liquid crystalline materials have a preferred orientation, typically described with a vector called the director, in an external electric field and their optical properties depend on this orientation.

Despite of the relatively long history, the complexity of these materials assures many more years of research for those interested to reveal the physics behind their extraordinary behaviour. A particular kind of liquid crystals, i.e. lyotropic liquid crystals, are also abundant in living systems, making this intriguing phase an interesting research subject for researchers on a wide range of disciplines.
Most NMR experiments are performed in liquid state solutions. The isotropic movement of molecules in liquid or gas phase obstructs the observation of anisotropic interactions and leaves only the isotropic averages of the corresponding magnetic interaction tensors to be observable in the NMR spectra. This leads to a loss of valuable information that could shed light on the details of the dynamics and structures of liquid crystal molecules. On the other hand, in an anisotropic environment, such as solid or liquid crystalline phases, the orientation of the molecules is no longer random. Thus, anisotropic spectral parameters, such as direct dipolar couplings, quadrupolar couplings and the anisotropies of nuclear shielding and spin-spin coupling tensors, can be observed in NMR experiments. Unfortunately, complications may arise from the wealth of anisotropic interactions in solid state, within and between the nearby molecules, that masks the fine structure of the spectra. At the same time, in liquid crystalline phases the anisotropic intramolecular interactions are retained in the NMR spectra, while the intermolecular couplings average out because of the molecular tumbling, resulting in better resolved spectra with more detectable fine structure.

Proton NMR spectroscopy was applied to the study of liquid crystals already in the early 1950s by Spence, Moses and Jain [3]. Due to high orientational order and relatively large size of the liquid crystal molecules, the proton spectra can still be rather complex, and the accuracy of the information about the magnetic properties of the liquid crystalline molecules is quite limited. This main problem with the proton LC NMR is clearly presented in Figure 1.1 showing a proton spectrum of an LC Phase IV measured in isotropic and anisotropic phases. These complications can be alleviated by using more advanced NMR methods, such as multiple quantum experiments, two dimensional NMR, local field experiments, variable angle spinning, or suitable combinations of these methods (See e.g. Refs. 4–9). Instead of directly detecting the liquid crystal spectrum, it is also possible to utilise probe atoms or molecules, e.g. noble gases [10–12], to obtain indirect information about the liquid crystalline phases. Simplification of a complex spectrum can also be carried out with suitable isotopic enrichment. For example, some of the protons can be replaced with deuterium nuclei and, due to simpler spectrum, deuterium NMR has indeed proven to be a feasible tool to study the ordering, structure and dynamics of liquid crystals [13–17]. In addition to proton and deuterium, carbon-13 is regularly utilised in the NMR studies of liquid crystals [5, 9].

As the behaviour of liquid crystals in external fields is the cornerstone of the applications of these materials in display technology, it is a research subject of great interest. The response of the liquid crystal director to external fields depends on several physical properties, such as the dielectric and diamagnetic anisotropies and the rotational viscosity coefficient. The main property to determine the response times of the LC displays is the rotational viscosity coefficient. Thus, several experimental methods, such as capacitance, transient current, optical, ESR and NMR measurements, as well as mechanical methods utilising torque measurements, have been developed to obtain this property [18–20]. As the director orientation is readily obtainable with deuterium NMR, this method has successfully been applied also to study the dynamics of the liquid crystal director in the presence of external electric and magnetic fields [21]. As the dipolar couplings contain information about the ordering, also the proton LC NMR have been utilised to study the
director rotation under the influence of external fields [22–25]. However, the generally simpler nature of deuterium NMR spectra provides more easily interpretable data.

1.1.4 LC NMR and Solute Molecules

In 1960s Saupe and Englert [26] introduced a new application of LC NMR; the study of properties of solute molecules dissolved into liquid crystalline solvents. Due to the ordering of the solvent molecules, also the solute molecules tend to have a preferred orientation and residual anisotropic spectral parameters can be observed in NMR experiments. These anisotropic parameters can then be utilised to obtain detailed information about, for example, the structure of the solvent molecules [27, 28].

During the last decades development of computers and computational theories has enabled researchers to perform state-of-the-art theoretical calculations of the NMR properties and thereby to obtain highly precise values independently from the experiments [29].
Thus, accurate experimental values are in need as a reference to evaluate the quality of the calculations. Complications arise from the fact that, in real life, molecules rotate, vibrate and interact with the surrounding solvent molecules. Thus, to obtain accurate and comparable experimental and theoretical values for the NMR parameters, a thorough consideration of these effects is in place both in the experiments and in the calculations.

The LC NMR method can certainly be expanded also to study the magnetic properties of not-so-small molecules, as has been done with the residual dipolar couplings in the structural studies of proteins [30–32]. However, the weakly orienting solvents utilised to avoid overly complicated spectra naturally lead to lesser obtainable information as some of the interactions cease to be experimentally observable. Furthermore, with the increasing size and mobility of the system, the treatment of motional averaging and solvent interactions can become extremely tedious task. Thus the obtainable accuracy of the NMR parameters is reduced.

1.2 Outline of the Thesis

This thesis consists of introductory and theoretical parts describing the background and some relevant theoretical points in connection with the current applications, as well as of brief summaries of the five journal articles representing the original work carried out for the thesis. Chapters 2 and 3 will briefly familiarise the reader with liquid crystals, theory of NMR as well as the combination of these two, namely the LC NMR. For a more thorough description of NMR the reader is advised to read, for example, the books by Abragam [33], Slichter [34], Levitt [35] or Ernst, Bodenhausen & Wokaun [36]. On top of the aforementioned books, the notations on the theory of NMR are partly based on the lecture notes by Docent Juhani Lounila [37–39]. More details on the theory of liquid crystals can be found, for example, from the books by Chandrasekhar [40], Collins & Hird [41] or Yang & Wu [42]. There are also good books focused specifically on the NMR of liquid crystals (See e.g. Refs. 43–45).

In the proceeding Chapters, 4 and 5, the thesis will deal with the experimental aspects of the original articles. Papers I and II introduced in Chapter 4 discuss the liquid crystal director dynamics in external fields as studied by deuterium NMR. Hence, the first part of the experimental work adds on to the long and profound research by the groups of Professors Geoffrey Luckhurst (University of Southampton, UK) and Akihiko Sugimura (Osaka-Sangyo Technical University, Japan) on the behaviour of liquid crystals in external electric and magnetic fields. Papers III, IV and V covered in Chapter 5 concentrate on the magnetic properties of small molecules and are based on the strong tradition of LC NMR by the group of Professor Jukka Jokisaari in Oulu. In Paper III the nuclear magnetic shielding of carbon and proton in methyl halides (\(\text{CH}_3\), \(X = F, Cl, Br, I\)) is studied, in Paper IV the subject is the carbon-mercury spin-spin coupling in methyl mercury halides (\(\text{CH}_3\text{HgX}\), \(X = Cl, Br, I\)) and Paper V concentrates on the deuterium quadrupole coupling tensor in deuterated benzenes (\(\text{C}_6\text{H}_5\text{D}\) and 1,3,5-\(\text{C}_6\text{H}_3\text{D}_3\)). For a more complete list of references directly related to the projects presented in the papers the reader is referred to the reference lists of the original articles. As the author had no part on the electronic structure calculations, Chapter 5 concentrates mostly on the experimental work and reviewing the results in comparison with the computational values.
2 Liquid Crystals

As stated in Chapter 1, liquid crystalline phase is a phase between the liquid and the solid state. Liquid crystals are generally divided into two classes; lyotropic and thermotropic. In addition, liquid crystals formed by polymers are quite often counted as a third class of liquid crystals [41]. Lyotropic materials are composed of two or more components, of which one is amphiphilic. Many lyotropic liquid crystals are of biological interest, but probably the most commonly known lyotropic liquid crystalline phase is made of soap and water. Thermotropic materials are pure compounds, or mixtures of pure liquid crystal compounds, that exhibit a liquid crystalline state within a certain temperature range. Thermotropic materials are usually composed of either flat, disk-like, or long, rod-like, molecules. Depending on the structure of the molecules, they can form different kinds of liquid crystalline mesophases. For rod-like thermotropic liquid crystals these phases are broadly classified as nematic, cholesteric and smectic. In the nematic phase the molecules prefer to orient along a certain direction, called the director (\( \hat{n} \)), but they show no additional spatial ordering. The cholesteric phase, also known as a chiral nematic phase, resembles the nematic phase, but it is composed of optically active molecules and has an axis of rotation perpendicular to the director, so that the orientation of the director twists about the axis. In the smectic phase there is also positional ordering as the molecules tend to congregate into layers. In addition, there exist sub-phases of the smectic phase depending on the ordering of the molecules within the layers. Schematic representations of the isotropic, nematic and smectic A phases are shown in Figure 2.1. The lyotropic materials can also be found in several different liquid crystalline phases, for example cubic, lamellar and hexagonal phases, but those will not be treated with more detail as all the liquid crystals employed in this theses were thermotropic, uniaxial, nematic, and calamitic, the last referring to rod-like molecules.

2.1 Orientational Order

Orientational order is probably the single most important property of the liquid crystals, as it is the cause of the anisotropic properties of these materials exploited in various applications. The ordering of a uniaxial nematic phase is commonly described with Saupe
order parameters,
\[ S_{\alpha\beta} \equiv \langle s_{\alpha\beta} \rangle = \langle (3 \cos \theta_{\alpha} \cos \theta_{\beta} - \delta_{\alpha\beta})/2 \rangle, \]
where $\alpha$ and $\beta$ are the molecular axis, angle $\theta$ describes the orientation of the axis with respect to the director, $\hat{n}$, and $\delta_{\alpha\beta}$ is Kronecker delta ($\delta_{\alpha\beta} = 1$ for $\alpha = \beta$ and $\delta_{\alpha\beta} = 0$ for $\alpha \neq \beta$). The angular brackets manifest the fact that the order parameter is calculated as an average over molecular motions. $S$ is a traceless ($\sum_{\alpha\beta} S_{\alpha\beta} = 0$) and symmetric ($S_{\alpha\beta} = S_{\beta\alpha}$) tensor. In the preceding equation, and henceforth, the instantaneous orientation is denoted with lower case letters, $s_{\alpha\beta}$ and the average orientation with capital letters, $S_{\alpha\beta}$.

For rigid, rod-like molecules forming a uniaxial nematic phase it is sufficient to consider only the orientation of the long molecular axis, usually denoted as $S_{zz}$. This is because, although the actual geometry of individual liquid crystal molecules might be of lower symmetry, effectively the molecules possesses cylindrical symmetry due to fast rotation around the long axis. Thus, the average molecular ordering of a calamitic uniaxial nematic phase can be described with
\[ S_{zz} = \langle (3 \cos^2 \theta - 1)/2 \rangle = \langle P_2(\cos \theta) \rangle, \]
where the angle $\theta$ describes the orientation of the long axis of the molecule with respect to the director, and $P_2$ is the second order Legendre polynomial. For a totally random, i.e. isotropic, orientation $S = 0$ and for a perfectly oriented system $S = 1$. For nematic liquid crystals $S$ is typically between 0.4 and 0.7 [46]. The description of positional order, e.g. for the smectic phases, would require additional parameters, but they are not covered here, as this thesis concentrates on uniaxial nematic liquid crystals. Naturally, Eqs. (2.1) and (2.2) are applicable also for solute molecules dissolved into liquid crystalline solvents.
Considerations of the flexibility of the molecules and the molecular symmetry are in order if the ordering of real liquid crystal molecules or non-rigid solutes are to be pursued, but as the current applications deal with rigid small solute molecules and, in case of the liquid crystal studies, only the director orientation is of interest, Eqs. (2.1) and (2.2) are well suited for these studies.

2.2 Liquid Crystals in External Fields

Although the liquid crystalline molecules possess preferred orientation along the director, in unconstrained environments this ordering is only local (or microscopic), as there is no preferred orientation of the directors within a bulk sample. On the contrary, when a liquid crystalline sample is put under the influence of an external magnetic or electric field, the local directors throughout the sample possess a common orientation with respect to the field and global (or macroscopic) ordering is obtained. This preferred orientation of the liquid crystal director, \( \hat{n} \), in an external electric or magnetic field depends on the sign of the anisotropy of the diamagnetic or dielectric susceptibility tensor, \( \Delta \chi \) or \( \Delta \epsilon \), respectively. For a positive anisotropy, the director has a tendency to orient parallel to the field and in case of a negative anisotropy, the director orients perpendicular to the field. For uniaxial nematic liquid crystals both the susceptibility tensors are cylindrically symmetric (i.e. \( \chi_x = \chi_y = \chi_\perp, \epsilon_x = \epsilon_y = \epsilon_\perp \)).

Application of an electric field, \( \mathbf{E} \), to a liquid crystal sample produces a polarisation, \( \mathbf{P} \), i.e. a dipole moment per unit volume. The tensor describing the relation between \( \mathbf{E} \) and \( \mathbf{P} \) is the aforementioned dielectric susceptibility tensor, \( \epsilon \), \(^1\) and the relation can be written as

\[
\mathbf{P} = \varepsilon_0 \epsilon \mathbf{E} = \varepsilon_0 \left[ \epsilon_\perp \mathbf{E} + \Delta \epsilon (\hat{n} \cdot \mathbf{E}) \hat{n} \right],
\]

where \( \varepsilon_0 \) is the permittivity of vacuum. In the latter equation, the dielectric susceptibility tensor is presented by means of the tensor components parallel, \( \epsilon_\parallel \), and perpendicular, \( \epsilon_\perp \), to the director and the anisotropy is defined as \( \Delta \epsilon = \epsilon_\parallel - \epsilon_\perp \). The electric field induced dipole moments on the molecules give their contribution to the polarisation, but unlike in the normal solid and liquid phases, the orienting forces of the electric field on the permanent dipole moments can be of substantial magnitude as well. The electric displacement field, \( \mathbf{D} \), is defined as

\[
\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon_0 (1 + \epsilon_\perp) \mathbf{E} + \varepsilon_0 \Delta \epsilon (\hat{n} \cdot \mathbf{E}) \hat{n}
\]

and the torque produced by the electric field on the director is

\[
\Gamma_E = \mathbf{D} \times \mathbf{E} = \varepsilon_0 \Delta \epsilon (\hat{n} \cdot \mathbf{E}) (\hat{n} \times \mathbf{E}).
\]

\(^1\)In literature a symbol \( \chi_E \) is also used for the dielectric susceptibility tensor to avoid confusion with the dielectric constant, for which symbol \( \epsilon \) is often used.
When the sample is exposed to an external magnetic field, $B$, the magnetic properties of the medium effect the local field just as the electric properties modify the external electric field. The relation between the magnetic field (also called the magnetic flux density) and the so called magnetising field (or the magnetic field strength), $H$, is

$$B = \mu_0 (1 + \chi) H,$$

(2.6)

where $\chi$ is the magnetic susceptibility tensor and $\mu_0$ is the permeability of vacuum. Analogously to the external electric field inducing polarisation, the magnetic field creates magnetisation, $M$, due to the weak magnetic dipole moments induced on the molecules;

$$M = \chi H = \left[ \chi_\perp H + \Delta \chi (\hat{n} \cdot H) \hat{n} \right].$$

(2.7)

Nematic liquid crystals in general have small negative magnetic susceptibilities ($\sim 10^{-5}$), thus they are diamagnetic. The magnetic interactions between the molecules are insignificant compared to their interaction with the external field. Because of this, the local field experienced by the liquid crystal molecules can quite safely be approximated by the external field when studying the ordering and the other properties of the liquid crystals. The magnetic torque can now be written as

$$\Gamma_M = M \times B = \mu_0 \Delta \chi (\hat{n} \cdot H) (\hat{n} \times H) \approx \frac{1}{\mu_0} \Delta \chi (\hat{n} \cdot B) (\hat{n} \times B).$$

(2.8)

To describe the dynamical behaviour of the director, it is generally necessary to invoke hydrodynamics. Hydrodynamical theories are based on the assumption that the fluid is a continuum and the relevant dynamic equations are derived utilising the conservation laws of mass, momentum and energy. According to the Newton’s second law (conservation of momentum), the equation of motion can be written as

$$\rho \frac{dv}{dt} = f,$$

(2.9)

where $v$ is the linear velocity, $\rho$ is the density and $f$ represents a general force per unit volume acting on the fluid. Depending on the conditions, this force contains separate contributions arising from surface interactions, viscosity effects, and external forces, such as electric or magnetic fields or gravitation. A general form of equation describing the motion of a fluid, the so called Navier-Stokes equation, can be written as

$$\rho \left( \frac{\partial v}{\partial t} + (\nabla \cdot v)v \right) = \nabla \cdot T + f,$$

(2.10)

where $T$ is a stress tensor describing the pressure effects and viscose dissipation and $f$ represents the body forces (per unit volume).

Unlike in isotropic liquids, in liquid crystals most physical properties and interactions are anisotropic and the dependence of the stress tensor and the body forces on the orientation and rotation of the director needs to be integrated into hydrodynamical equations. Thus, when describing the ordering of the nematic phase, the hydrodynamics is
combined with the elastic continuum theory for nematic liquid crystals. The theory of
hydrodynamics in nematics has been developed principally by Leslie [47–49] and Ericksen
[50–52], thus it is traditionally called Leslie-Ericksen (or Ericksen-Leslie) continuum
theory [40, 42].

In nematic phases, the minimum energy is reached with uniform director orientation.
In real life, the orientation of the director may vary spatially because of, for example,
surface interactions with the container or interactions with an external field. This effect is
called the deformation of the director, or the elastic deformation. These deformations are
divided into three classes, splay, twist and bend, and they are described with correspond-

\[ f_1, f_2 \text{ and } f_3. \]

These forces, and further the energy needed for elastic deformations, are typically written in terms of the so called Frank elastic constants, \( K_{11}, K_{22} \) and \( K_{33}. \)

In confinement, the surfaces of the container often promote either homogeneous (par-
allel) or homeotropic (perpendicular) anchoring of the liquid crystal molecules. The im-
portance of the anchoring effects on the director orientation of the sample then depends
on the strength of the anchoring as well as the size and shape of the sample.

When considering the effects of external fields on the ordering of the director, the
sample can be expected to behave as a bulk if the magnetic coherence length,

\[ \xi_M = \frac{1}{B} \sqrt{\frac{\mu_0 K}{\Delta \chi}}, \quad (2.11) \]

and the electric coherence length,

\[ \xi_E = \frac{1}{E} \sqrt{\frac{K}{\varepsilon_0 \Delta \varepsilon}}, \quad (2.12) \]

are small compared to the sample dimensions – like the cell thickness in case of a flat
sample cell. In strong homogeneous magnetic and electric fields the director orientation
in a large sample container is, to a good approximation, uniform and both the surface
anchoring and the elastic deformations can be disregarded.

In liquid crystalline medium, also the viscosity depends on the orientation of the direc-
tor. In general, the viscous forces include contributions from the translational viscosity
as well as the rotational viscosity. However, as the practical applications in this thesis deal
with director rotation of an otherwise static sample (\textit{i.e.} no flow), translational viscosity
will be ignored in the following. Generally, the torque \( \Gamma \) by a body force \( f \) on the director
is \( \hat{n} \times f \) and the torque by the pure rotational viscosity can be written as [42]

\[ \Gamma_{\text{vis}} = -\hat{n} \times \gamma_1 \mathbf{N}, \quad (2.13) \]

where \( \gamma_1 \) is the rotational viscosity coefficient. In Eq. (2.13) \( \mathbf{N} \) is the net angular velocity
of the local director with respect to the background fluid;

\[ \mathbf{N} = (\Omega - \omega) = \frac{d\hat{n}}{dt} - \omega \times \hat{n}, \quad (2.14) \]

where \( \Omega \) is the local angular velocity of the director and \( \omega \) is the angular velocity of the
background.
For a rotating sample the equation of motion describing the angular acceleration, \( d\Omega/dt \), of the director axis can now be written as

\[
I \frac{d\Omega}{dt} = \Gamma_{\text{ext}} + \Gamma_{\text{vis}},
\]

(2.15)

where \( I \) is the moment of inertia per unit volume. For most practical experiments, the director dynamics is overdamped and the director inertia can be neglected [42, 53]. Thus, only the viscosity torque and the torques by the external fields are retained in Eq. (2.15). As a consequence, the torque by the external fields is balanced by the viscous torque and we finally end up with a simple torque-balance equation;

\[
\Gamma_{\text{ext}} + \Gamma_{\text{vis}} = 0.
\]

(2.16)
3 Nuclear Magnetic Resonance

Magnetic nuclei, that is all the nuclei that do not have an even number of both the protons and the neutrons, have an intrinsic feature called the nuclear spin. The nuclear spin has little effect on the molecular properties, but nevertheless provides a feasible tool to study these properties. This stems from the fact that the nuclear magnetic interactions are weak compared to the cohesive forces keeping the bits and pieces of the molecule together – making NMR an indestructible research method – but nevertheless contain a wealth of information about the nuclear environment, that is the electronic structure and the nearby nuclei. These nuclear magnetic interactions can be studied by placing the sample into an external magnetic field, disturbing the system with a radio frequency radiation of suitable frequency, and observing the following response as the system returns to its equilibrium state.

3.1 NMR Interactions

A nucleus $i$ with a spin angular momentum ($\mathbf{I}_i \neq \mathbf{0}$) has a magnetic dipolar moment, $\mathbf{\mu}_i$, that can be written as

$$\mathbf{\mu}_i = \gamma_i \hbar \mathbf{I}_i,$$

(3.1)

where $\gamma_i$ is the gyromagnetic ratio of the nucleus, $\hbar$ is the Planck’s constant, $\hbar$, divided by $2\pi$ and $\mathbf{I}_i$ is the unitless spin angular momentum vector. Both the size and the direction of the vector $\mathbf{I}_i$ are quantised, i.e. they can only get discrete values that depend on the spin quantum number of the nucleus, $I_i$. A nucleus in a magnetic field interacts with the external field as well as with the electrons and the other nuclei. This gives rise to the Zeeman interaction, the nuclear magnetic shielding, the direct dipolar coupling, the indirect spin-spin coupling and the quadrupolar coupling. All the interactions can be described with suitable second rank tensors and the spectral parameters directly bound to these interactions can be extracted from the experimental NMR spectra.

A nucleus in a static external magnetic field ($\mathbf{B}_0$) has a magnetic interaction energy

$$E = -\mathbf{\mu}_i \cdot \mathbf{B}_0 = -\gamma_i \hbar I_i I Z B_0,$$

(3.2)
where $I_{iZ}$ is the $Z$-component of the spin angular momentum vector $I_i$. The latter formulation is valid, if the $Z$-axis is chosen to be along the direction of the magnetic field. When expressed in the frequency units, the corresponding energy operator, \textit{i.e.} the Hamilton operator, is

$$\hat{H}_0 = -\frac{\gamma_i}{2\pi} B_0 \hat{I}_{iZ} = -\nu_{i0} \hat{I}_{iZ}. \quad (3.3)$$

This interplay between the magnetic moment of the nucleus and the external magnetic field is called the Zeeman interaction. Since the value of $\gamma_i$ depends on the nucleus, it is the source of the characteristic frequencies, so called Larmor frequencies, $\nu_{i0}$, typical for each type of nucleus. With modern high field spectrometers these frequencies are typically in megahertz range (10-1000 MHz).

However, the local magnetic field at the nucleus deviates from the static field $B_0$, as the electrons surrounding the nucleus shield the external magnetic field. The effect the electrons have on the magnetic field at the nucleus can be described with the nuclear shielding tensor, $\sigma_i$, and the corresponding Hamiltonian can be written as

$$\hat{H}_\sigma = \frac{\gamma_i}{2\pi} \mathbf{I}_i \cdot \sigma_i \cdot B_0. \quad (3.4)$$

The direct dipolar interaction between the dipolar moments of two nuclei, $i$ and $j$, can be described with the Hamiltonian

$$\hat{H}_{D} = \mathbf{I}_i \cdot \mathbf{D}_{ij} \cdot \mathbf{I}_j , \quad (3.5)$$

where $\mathbf{D}_{ij}$ is the dipolar coupling tensor, which is purely anisotropic, \textit{i.e.} it can only be observed in an anisotropic phase.

Like the electrons within the molecule shield the external magnetic field they also shield the direct dipole-dipole interaction. This interaction is called the indirect spin-spin interaction and the corresponding Hamiltonian is of a same form as the dipolar Hamiltonian, namely

$$\hat{H}_{J} = \mathbf{I}_i \cdot \mathbf{J}_{ij} \cdot \mathbf{I}_j , \quad (3.6)$$

where $\mathbf{J}_{ij}$ is the spin-spin coupling tensor. Unlike the dipolar coupling tensor, $\mathbf{J}_{ij}$ contains both the isotropic and the anisotropic parts.

The quadrupole moment, $eQ_i$, of a quadrupolar nucleus ($I_i \geq 1$) interacts with the electric field gradient (EFG) at the nuclear site. This leads to an NMR observable quadrupole splitting. The relevant interaction Hamiltonian can be expressed in a familiar form as

$$\hat{H}_Q = \mathbf{I}_i \cdot \mathbf{Q}'_i \cdot \mathbf{I}_i , \quad (3.7)$$

where

$$Q'_i = \frac{eQ_i}{2\hbar I_i(2I_i - 1)} V_i \equiv \frac{\chi_i}{2I_i(2I_i - 1)}. \quad (3.8)$$

In Eq. (3.8) $I_i$ has it usual meaning as the spin quantum number of the nucleus $i$ and $V_i$ is the EFG tensor. In the latter formulation

$$\chi_i = eQ_i V_i / \hbar \quad (3.9)$$
is the quadrupolar coupling tensor regularly used instead of the EFG tensor.\footnote{Despite the risk of confusion, symbol $\chi$ is used both for the quadrupolar coupling and for the magnetic susceptibility as it is the recommendation by IUPAC \cite{54,55}} Like the dipolar coupling tensor, the quadrupolar coupling tensor is purely anisotropic.

Finally, if we consider the whole spin system, we have to add up all the contributions and calculate a sum over all the spins and the spin pairs. So, we can write the total Hamiltonian as

$$\hat{H}_{\text{tot}} = \sum_i (\hat{H}_{i0} + \hat{H}_{si} + \hat{H}_{Qi}) + \sum_{i<j} (\hat{H}_{D_{ij}} + \hat{H}_{J_{ij}}).$$

(3.10)

### 3.2 Spectral Parameters in NMR

In general, any second rank tensor, $\mathbf{F}$, can be divided into isotropic and anisotropic parts as

$$\mathbf{F} = \mathbf{F}^{\text{iso}} + \mathbf{F}^{\text{aniso}} = \mathbf{F}^{\text{iso}} + \mathbf{F}^{\text{aniso}} = \mathbf{1} + \mathbf{F}^{\text{aniso}},$$

(3.11)

where $\mathbf{1}$ is the unit tensor ($1_{\alpha\beta} = \delta_{\alpha\beta}$). It is a widespread convention to report the tensorial properties of the NMR interaction tensors by using the parameters known as the isotropy, $F^{\text{iso}}$, the anisotropy, $\Delta F$, and the asymmetry parameter, $\eta$. These parameters are typically defined in a suitable molecule fixed frame ($x, y, z$) as

$$F^{\text{iso}} = \frac{1}{3} (F_{xx} + F_{yy} + F_{zz}),$$

(3.12)

$$\Delta F = \frac{3}{2} F^{\text{aniso}} = [(F_{zz} - \frac{1}{2} (F_{xx} + F_{yy})] \quad \text{and}$$

(3.13)

$$\eta = \frac{F_{xx} - F_{yy}}{F_{zz}},$$

(3.14)

although there are also other definitions of the asymmetry parameter.\footnote{Especially in the solid state NMR, the asymmetry parameter is sometimes defined as $\eta = (F_{xx} - F_{yy})/(F_{zz} - F)$ \cite{56}. Instead of the asymmetry parameter, rhombicity, $R$, is sometimes used, but its definition varies. For example $R = (F_{yy} - F_{xx})$ or $R = \frac{2}{3} (F_{xx} - F_{yy})/F_{zz}$.} The asymmetry parameter can obtain values between 0 and 1 and for a cylindrically symmetric tensor ($F_{xx} = F_{yy}$) the asymmetry parameter is zero. For any real, symmetric tensor, it is possible to find principal axis system (PAS), where the matrix representation of this tensor is diagonal, thus it only contains the elements $F_{xx}, F_{yy}$ and $F_{zz}$. The coordinate system is often chosen in such a way that $|F_{xx}| \leq |F_{yy}| \leq |F_{zz}|$. The isotropic part, i.e. one third of the trace of the tensor, is a constant irrespective of the coordinate system. Quite the contrary, the anisotropy and the asymmetry parameter are orientation dependent quantities, thus it is important to define the relevant coordinate system in which the values for these parameters are reported.

The magnetic interaction tensors are molecular properties, but in NMR experiments they are observed with respect to the laboratory-fixed frame ($B_0||Z$). Thus, the NMR observables are the components of these tensors along the $Z$−axis, calculated as motional averages over all the molecules in the sample, $\langle F_{iZZ} \rangle$. 
In case of uniaxial nematic liquid crystals the orientation of the liquid crystal director with respect to the external magnetic field can be described with a single parameter, \( i.e. \) the second order Legendre polynomial, \( P_2(\cos \theta) \), where \( \theta \) is the angle between the liquid crystal director and the external magnetic field. For liquid crystals orienting parallel or perpendicular to the magnetic field \( P_2(\cos \beta) \) adopts a value of \( 1 \) or \(-1/2\), respectively. The NMR parameters, \( F^{\text{exp}} \), observed in uniaxial nematic liquid crystalline solvents can now be written as

\[
F^{\text{exp}} = \langle F_{ZZ} \rangle = \frac{1}{3} \sum_{\alpha} F_{\alpha \alpha} + \frac{2}{3} P_2(\cos \theta) \sum_{ab} F_{ab} S_{ab}^n
\]

\[
= F^{\text{iso}} + \frac{2}{3} P_2(\cos \theta) [\Delta F_{zz} S_{zz}^n + \frac{1}{2} (F_{xx} - F_{yy}) (S_{xx}^n - S_{yy}^n)] + (F_{xy} + F_{yx}) S_{xy}^n + (F_{xz} + F_{zx}) S_{xz}^n + (F_{yz} + F_{zy}) S_{yz}^n, \tag{3.15}
\]

where the molecular orientation parameters \( S_{\alpha \beta}^n \) (See Eq. (2.1)) are defined with respect to the liquid crystal director, \( \hat{n} \). As the anisotropic part in Eq. (3.15) is related to the orientation tensor, \( S \), the motional average of this component in the laboratory frame disappears if calculated over a fully random movement of molecules representing, \( i.e. \) a normal liquid or gas phase or the isotropic phase of the LC solvent.

The number of independent molecule-fixed tensor elements, \( F_{ab} \), and orientation parameters, \( S_{ab}^n \), depends on the chosen coordinate system as well as on the molecular symmetry. If the tensor elements \( F_{ab} \) in Eq. (3.16) are defined in the PAS of this tensor, or in the PAS of the orientation tensor, only the isotropic part \( F^{\text{iso}} \) and the terms containing the elements \( F_{xx}, F_{yy} \) and \( F_{zz} \) are retained and Eq. (3.16) simplifies to

\[
F^{\text{exp}} = F^{\text{iso}} + \frac{2}{3} P_2(\cos \theta) [\Delta F_{zz} S_{zz}^n + \frac{1}{2} (F_{xx} - F_{yy}) (S_{xx}^n - S_{yy}^n)] . \tag{3.17}
\]

Furthermore, if either of the tensors, \( F \) or \( S^n \), is cylindrically symmetric in this coordinate system \( (F_{xx} = F_{yy} \) or \( S_{xx} = S_{yy} \)), only the first element of the anisotropic part remains and the equation further reduces to

\[
F^{\text{exp}} = F^{\text{iso}} + \frac{2}{3} P_2(\cos \theta) \Delta F_{zz} S_{zz}^n . \tag{3.18}
\]

The NMR observable component of the shielding tensor can now be written as

\[
\sigma_i \equiv \langle \sigma_{iZZ} \rangle = \frac{1}{3} \sum_{\alpha} \sigma_{i\alpha\alpha} + \frac{2}{3} P_2(\cos \theta) \sum_{ab} \sigma_{iab} S_{ab}^n . \tag{3.19}
\]

Instead of the shielding tensor components, it is often sufficient to study the chemical shift, \( \delta \), \( i.e. \) the shielding with respect to the shielding of a chosen reference;

\[
\delta = (\sigma_{\text{ref}} - \sigma_i)/(1 - \sigma_{\text{ref}}) \approx \sigma_{\text{ref}} - \sigma_i . \tag{3.20}
\]

The last formulation is valid if \( |\sigma_{\text{ref}}| \ll 1 \), which is true in many cases as the shieldings are typically in ppm (parts per million) range, especially for the lighter elements such as hydrogen and carbon.

Following the same procedure, the observable dipolar coupling is

\[
\langle D'_{ijZZ} \rangle \equiv 2 D_{ij} , \tag{3.21}
\]
where $D_{ij}$ is the dipolar coupling constant, which can be written as

$$D_{ij} = -P_2(\cos \theta) \frac{\mu_0 \gamma_i \gamma_j}{8\pi^2} S_{ij}^n,$$  \hspace{1cm} (3.22)

Here $S_{ij}^n = \frac{1}{2} \langle \cos^2 \theta \rangle - \frac{1}{4}$ is the order parameter of the internuclear vector $r_{ij}$. From Eq. (3.22) it is evident that the dipolar couplings contain information about both the molecular structure and the orientation.

As with the previous interaction tensors, the NMR observable component of the spin-spin coupling tensor is the average $\langle J_{ij}^{\text{Z}_Z} \rangle$, which can be further divided into isotropic and anisotropic contributions, $J_{ij}^{\text{iso}}$ and $J_{ij}^{\text{aniso}}$, respectively. The isotropic part, $J_{ij}^{\text{iso}} \equiv J_{ij}$, is called the spin-spin coupling constant.

The NMR observable quadrupole coupling can be written as

$$\langle Q'_{Z_1} \rangle = \frac{P_2(\cos \theta)}{2I_i(2I_i - 1)} \sum_{ab} \chi_{iab} S_{ab}^n \equiv \frac{1}{3} \Delta \nu_{iQ},$$  \hspace{1cm} (3.23)

where $\Delta \nu_{iQ}$ is used to denote the observable quadrupolar splitting. The nuclear quadrupole coupling constant (NQCC) with respect to the molecule-fixed $z-$axis is defined as the quadrupolar coupling tensor element along this axis,

$$\chi_{zz} = \frac{eQV_{zz}}{h}.$$  \hspace{1cm} (3.24)

In most cases the interaction energies related to the nuclear shielding, dipole-dipole coupling, spin-spin coupling and quadrupolar interactions are low compared to the Zeeman interaction, $\hat{H}_0$, thus can be treated as small perturbations. If only the energy terms preserved in the first order perturbation theory are taken into account, i.e. so called high field (or secular) approximation is used, the total Hamiltonian presented in Eq. (3.10) can be written as

$$\hat{H}_{\text{tot}} = -\sum_i \nu_i (1 - \sigma_i) \hat{I}_i + \frac{1}{2} \sum_i \Delta \nu_{iQ} \hat{I}_i^2 + \sum_{i<j} J_{ij} \hat{I}_i \cdot \hat{I}_j + \sum_{i<j} (D_{ij} + \frac{1}{2} J_{ij}^{\text{aniso}})(3\hat{I}_i \hat{I}_j - \hat{I}_i \cdot \hat{I}_j).$$  \hspace{1cm} (3.25)

The energy levels, and thereby the transitions between these levels, i.e. the NMR spectrum, of a spin system can now be specified by calculating the expectation values of a suitable Hamiltonian, $\langle m | \hat{H} | n \rangle$, in the basis of the eigenstates of the unperturbed (Zeeman) Hamiltonian, $\hat{H}_0$.

### 3.3 Rovibrational Effects and Solvent Interactions

The molecules within a sample do not only have rotational and translational, but also vibrational degrees of freedom. Thus Eqs. (3.17) and (3.18) should more precisely be written as

$$F^{\text{exp}} = \langle F^{\text{iso}} \rangle + \frac{2}{3} P_2(\cos \theta) \left[ \langle \Delta F_{zz} s_{zz}^n \rangle + \frac{1}{2} \langle (F_{xx} - F_{yy})(s_{xx}^n - s_{yy}^n) \rangle \right].$$  \hspace{1cm} (3.26)
and
\[ F^{\text{exp}} = \langle F^{\text{iso}} \rangle + \frac{2}{3} P_2(\cos \theta) \langle \Delta F_{zz} s_{zz}^n \rangle. \] (3.27)

Now the angular brackets \( \langle \rangle \) are used to represent both the calculation over all the spins in the sample as well as the motional averaging, including the rovibrational motions. Thereby also the isotropy is denoted as an average. Placing the tensor elements and the orientation parameters inside the same angular brackets \( \langle F_{\alpha \beta}, s_{\alpha \beta} \rangle \neq \langle F_{\alpha \beta} \rangle \langle s_{\alpha \beta} \rangle \) manifests the solvent induced rotation-vibration coupling that will be discussed in more detail in Section 3.3.2.

In general, if only small-amplitude motions are present, the experimentally observable NMR property, \( F^{\text{exp}} \), can be divided into separate contributions [57–59]:
\[ F^{\text{exp}} = F^e + F^h + F^{\text{ah}} + F^{\text{cf}} + F^d, \] (3.28)
where \( F^e \) refers to the value in the equilibrium geometry, \( F^h \) and \( F^{\text{ah}} \) are the contributions arising from the harmonic and anharmonic vibrations, respectively, \( F^{\text{cf}} \) is the centrifugal contribution and \( F^d \) refers to the aforementioned rotation-vibration coupling, also called the deformation contribution.

### 3.3.1 Rovibrational Effects

The effect of the rovibrational motions on a property \( F \) at a finite temperature, \( T \), can be described using a Taylor series expansion of the property in terms of the normal coordinates, \( Q_k \), around the equilibrium geometry, \( r_e \), and calculating a thermal average of this expansion [60]:
\[ \langle F_{\alpha \beta} \rangle^T = F_{\alpha \beta}^e + \sum_k (F_{\alpha \beta,k})^e \langle Q_k \rangle^T + \frac{1}{2} \sum_{kl} (F_{\alpha \beta,kl})^e \langle Q_k Q_l \rangle^T + \ldots . \] (3.29)

In Eq. (3.29) \( F_{\alpha \beta,k} \) and \( F_{\alpha \beta,kl} \) are shorthand notations for the derivatives,
\[ (F_{\alpha \beta,k})^e \equiv \left. \frac{\partial F_{\alpha \beta}}{\partial Q_k} \right|_e \quad \text{and} \quad (F_{\alpha \beta,kl})^e \equiv \left. \frac{\partial^2 F_{\alpha \beta}}{\partial Q_k \partial Q_l} \right|_e, \] (3.30)
calculated at the \( r_e \) geometry. In general, the expansion converges rapidly for rigid molecules and only the linear and the quadratic terms are retained. The thermal averages \( \langle Q_k Q_l \rangle^T \) are obtained from the harmonic force field and \( \langle Q_k \rangle^T \) from the anharmonic force field.

The harmonic contribution at temperature \( T \) can be written as [59]
\[ \langle F_{\alpha \beta}^h \rangle^T = \frac{\hbar}{4} \sum_k F_{\alpha \beta,kk}^h \frac{1}{\omega_k} \coth \left( \frac{\hbar \omega_k}{2k_B T} \right). \] (3.31)
In Eq. (3.31) \( k_B \) is the Boltzmann constant and \( \omega_k = 2\pi \nu_k \) is the \( k \)th vibrational angular frequency. According to Eq. (3.15), in a uniaxial liquid crystal environment the NMR observable harmonic contribution would then be
\[ F^h = \frac{1}{3} \sum_\alpha \langle F_{\alpha \alpha}^h \rangle^T + \frac{2}{3} P_2(\cos \theta) \sum_{\alpha \beta} \langle F_{\alpha \beta}^h \rangle^T S_{\alpha \beta}^n. \] (3.32)
Similarly, the cubic force field can be utilised to calculate the thermal averages \( \langle Q_k \rangle^T \)
in Eq. (3.29) to obtain the anharmonic corrections, provided that the property derivatives are obtainable, and the anharmonic contribution at a finite temperature can be written as [58]

\[
\langle F_{\alpha\beta}^{\text{ah}} \rangle^T = -\frac{\hbar}{4} \sum_{kl} F_{\alpha\beta,k}^{\text{ah}} \frac{1}{\omega_k^2} \frac{\Phi_{kll}}{\omega_l} \coth \left( \frac{\hbar \omega_l}{2k_B T} \right),
\]

(3.33)

where \( \Phi_{kll} \) are the cubic anharmonic force constants (in normal coordinates). Another feasible means to include the anharmonic effects and the centrifugal corrections is to expand the series in Eq. (3.29) around the effective \( r_\alpha(T) \) geometry [58], which represents the average positions of the atoms of a molecule at temperature \( T \). Effectively this means that the relevant NMR property is obtained at the \( r_\alpha \) geometry,

\[
F^{\alpha} = F^{\text{eq}} + F^{\text{ah}} + F^{\text{cf}},
\]

(3.34)

and only the harmonic corrections and deformation effects need to be treated separately.

### 3.3.2 Solvent Effects

Until now we have discussed the nuclear magnetic interactions within a molecule as well as between the nuclei and the external magnetic field. In real life NMR experiments, also the sample itself gives a contribution to the magnetic field and the molecules can interact with each other. Thus, the actual experimental tensors should more precisely be written as

\[
F^{\text{tot}} = F^{\text{m}} + F^{\text{b}} + F^{\text{l}},
\]

(3.35)

where the \( F^{\text{m}} \) is the molecular interaction tensor of an isolated molecule and \( F^{\text{b}} \) and \( F^{\text{l}} \) represent the contributions arising from the bulk and local solvent effects, respectively.

The bulk solvent effect arises from the macroscopic magnetic susceptibility of the solvent, so that the local magnetic field can be written as \( B = [1+(1/3-\kappa)\chi_v]B_0 \), where \( \chi_v \) is the volume magnetic susceptibility tensor and \( \kappa \) is the shape factor describing the geometry of the sample. For homogenous samples \( \chi_v = \text{constant} \) and for long cylindrical samples \( \kappa \approx 0 \), whereas for spherical samples \( \kappa = 1/3 \). The bulk solvent contribution has a similar effect on all the solute molecules, thus it does not effect, for example, the chemical shifts that are calculated as differences between the absolute shieldings. In addition, the bulk solvent effects do not change the coupling parameters any more than taking a sample from one magnet to another with a different field strength, because it just modifies the local magnetic field experienced by the molecules within the sample. The bulk solvent effects do induce a change in the nuclear shielding when switching between different solvents or gaseous and liquid phases. On the other hand, these effects are also easily eliminated by using an internal reference and observing chemical shifts, instead of absolute shieldings. Furthermore, when using an external reference it is possible to correct the chemical shifts for the bulk solvent effects, if the shapes of the containers and the magnetic susceptibilities of the samples are known.

In the studies on the nuclear shielding tensors the local effects are typically further divided into different contributions. Often a separation into terms arising from the molecular
susceptibility of the nearby molecules (also called the microscopic bulk effect), the van der Waals interactions and the electrostatic interactions is carried out and the contribution from the local solvent effects is written as [61]

\[ F_l = F^a + F^w + F^E. \] (3.36)

The microscopic bulk effect, \( F^a \), arises from the anisotropy in the magnetic susceptibility of the solvent molecules; when considering short-range interactions, most solvent molecules are non-spherical and have a molecular diamagnetic susceptibility, thus have a preferred orientation with respect to the solute molecule. This naturally affects the local magnetic field the solute molecule experiences. The last term \( F^E \) applies for polar solvents as it is caused by the charge distribution in the neighbouring solvent molecules creating an electric field acting on the solute. On top of the above-mentioned contributions, also strong specific interactions, such as hydrogen bonding, can occur.

One of the most striking examples of the solvent effects can be seen in xenon NMR spectroscopy; for this spherically symmetric single atom the chemical shift range of the isotopomer \( ^{129}\text{Xe} \) is spread over hundreds of ppm and, despite of the symmetry, the quadrupolar isotope \( ^{131}\text{Xe} \) shows rather large quadrupolar splittings when dissolved into an anisotropic environment. Evidence of the local solvent effects on the coupling parameters can also be seen in proton NMR spectra of methane (\( \text{CH}_4 \)) dissolved into LC solvents. Even though the dipolar couplings of methane in an anisotropic environment should disappear due to molecular symmetry, in some nematic LC solvents couplings of more than 10 Hz for \( D_{\text{CH}} \) and 1 Hz for \( D_{\text{HH}} \) can easily be observed.

One approach to describe these local solvent effects is the deformation theory developed by Lounila et al. [59, 62–64]. In this theory the internal and reorientational motions of the molecules are correlated, i.e. the orientation and the vibrational state of a molecule are considered to be interdependent with each other. In consequence of this correlation, for example, the dipolar coupling (See Eq. (3.22)) should more precisely be re-written as

\[ D_{ij} = -P_2(\cos \theta) \frac{\mu_0 \gamma_i \gamma_j}{8\pi^2} \left\langle \frac{s_{ij}^n}{r_{ij}^3} \right\rangle. \] (3.37)

Thus, as long as it is unknown how the vibrational motions, and thereby the average bond lengths, \( \left\langle r_{ij} \right\rangle \), are connected to the reorientational motions, \( \left\langle s_{ij} \right\rangle \), there is no way to obtain genuine orientation or geometric parameters from the experimental dipolar couplings.

In the deformation theory by Lounila et al. the anisotropic forces acting on a molecule are be described with an external anisotropic potential energy, \( U^{\text{ext}} \), which can be approximated with

\[ U^{\text{ext}} = -\sum_{ab} A_{ab} s_{ab}. \] (3.38)

Here the interplay between the solvent molecules and the solute is described with an anisotropic, second-rank interaction tensor, \( A \). According to classical Boltzmann statistics, the ordering tensor is

\[ S_{\alpha\beta}^n = \frac{1}{Z} \int s_{\alpha\beta} \exp[-U^{\text{ext}}/(k_B T)] d\Omega, \] (3.39)

where \( Z = \int \exp[-U^{\text{exp}}/(k_B T)] d\Omega \) and the integrals are calculated over all the molecular orientations \( \Omega \). Thus, if the interaction tensor is know, it can be used to calculate
the orientation tensor from Eq. (3.39). Now the deformation contribution on the tensor
element along the magnetic field can be calculated using equation

\[ F^{\text{el}} = \frac{1}{3} \sum_k \omega_k^2 \sum_{\alpha\beta\gamma} F_{\gamma\gamma,k} A_{\alpha\beta,k} S_{\alpha\beta}^n \]

\[ + P_2(\cos \theta) \sum_k \omega_k^2 \left[ \frac{1}{5} \sum_{\alpha\beta} F_{\alpha\beta,k} A_{\alpha\beta,k} \right. \]

\[ + \left. \frac{4}{21} \sum_{\alpha\beta\gamma} (3F_{\alpha\gamma,k} A_{\beta\gamma,k} - F_{\gamma\gamma,k} A_{\alpha\beta,k}) S_{\alpha\beta}^n \right] , \quad (3.40) \]

where, following the previous convention adopted in Eq. (3.29), \( F_{\alpha\beta,k} \) and \( A_{\alpha\beta,k} \) are the
derivatives of \( F_{\alpha\beta} \) and \( A_{\alpha\beta} \) with respect to a normal coordinate \( Q_k \). For example, for the
dipolar coupling the deformation contribution presented in Eq. (3.40) can be written as

\[ D_{\alpha\beta}^{ij} = -P_2(\cos \theta) \frac{\mu_0 h \gamma \gamma}{8\pi^2} \sum_k \omega_k^2 \left[ \frac{3}{10} \sum_{\alpha\beta} \phi_{\alpha\beta,k}^ij A_{\alpha\beta,k} \right. \]

\[ + \left. \frac{4}{21} \sum_{\alpha\beta\gamma} \left( 3\phi_{\alpha\gamma,k}^ij A_{\beta\gamma,k} - \phi_{\gamma\gamma,k} A_{\alpha\beta,k} \right) S_{\alpha\beta}^n \right] , \quad (3.41) \]

where \( \phi_{\alpha\beta}^ij \) is

\[ \phi_{\alpha\beta}^ij = \frac{\cos \theta_{ij,\alpha} \cos \theta_{ij,\beta}}{r_{ij}^3} \quad (3.42) \]

and \( \theta_{ij,\alpha} \) is the angle between the \( ij \)-bond and \( \alpha \)-axis.

For practical applications of the deformation theory, the interaction tensor \( A \) is generally overly complicated and its functional form is unknown. Using the bond-additivity model, the interaction tensor can be divided into independent bond interaction tensors, \( A_{ij} \), describing the torques acting on individual bonds between the nuclei \( i \) and \( j \):

\[ A = \sum_{i<j} A_{ij} . \quad (3.43) \]

Furthermore, like with any anisotropic and symmetric second-rank tensor, the bond interaction tensors can be described using the anisotropy, \( \Delta A_{ij} \), and the asymmetry, \( \eta_{ij} \), of these tensors. If only these two parameters are used, it is assumed that the forces acting on the bonds tend just to bend the whole segment, not to stretch the bond. In a general case, also the elongation of the bond can be included into the theory and an additional parameter, the derivative, \( \Delta A_{ij}' \), is needed. On the other hand, if cylindrically symmetric, rigid bonds are assumed, the anisotropy of the tensor is the only parameter needed to fully describe the interaction. Within the accuracy of the theory, this is often a valid approximation and it has been observed that, at least in some cases, the forces that tend to stretch the bonds indeed do not have as a significant contribution on the deformation of the molecules as the bending forces and do not have to be taken into account to explain the experimental results [63].

If achievable, after combining all the aforementioned vibrational and solvent effects, presented in Eqs. (3.32), (3.34), and (3.40), and in case of the shielding tensor adding the
bulk solvent effects, it is possible to obtain genuine molecular properties corresponding to $r_e$ or $r_\alpha$ geometries from the NMR experiments.

### 3.4 Spin Density Operator

In the NMR experiments we observe properties of an ensemble rather than a single spin. Thus it is often worthwhile to turn to quantum statistical mechanics. The spin density matrix, $\rho$, contains complete information about the ensemble of spins at a certain time. The diagonal elements of the spin density matrix, $\rho_{ii}$, represent the probabilities of the eigenstates and are called the spin populations. The off-diagonals, $\rho_{ij}$, connect pairs of different states and are called (phase) coherences. Generally the matrix representation of the spin density operator is given in the basis set, $|i\rangle$, formed by the eigenfunctions of the Zeeman Hamiltonian (see Eq. (3.3)) and in this basis set the equilibrium spin density matrix, $\rho_e$, has a simple diagonal form. The corresponding operator can be written as

$$\hat{\rho}_e = \frac{1}{2} (\mathbb{1} + \epsilon \hat{I}_Z),$$

where $\epsilon = \gamma \hbar B / k_B T$ and $\mathbb{1}$ is the unit operator. The time evolution of the system can be calculated by unitary transformations of the spin density matrix with the appropriate spin Hamiltonian, i.e. utilising the time evolution operator

$$\hat{U}(t + t_0, t_0) = \exp \left( -i 2\pi \int_{t_0}^{t_0 + t} \hat{H}(t') dt' \right).$$

(3.45)

Under the influence of this operator the spin density operator, $\hat{\rho}(t_0)$, evolves as

$$\hat{\rho}(t + t_0) = \hat{U}(t + t_0, t_0) \hat{\rho}(t_0) \hat{U}^{-1}(t + t_0, t_0).$$

(3.46)

The effect of the radio frequency pulses applied to the system in the NMR experiments can be described with special time evolution operators, i.e. the rotation operators:

$$R_a(\beta) = \exp(-i\beta \hat{I}_a),$$

(3.47)

where $a$ denotes the axis of rotation ($X$, $Y$) and $\beta$ is the pulse flip angle. For example, a $\frac{\pi}{2}$-pulse around the $X$-axis would be denoted $R_X(\frac{\pi}{2})$. 
4 Liquid Crystal Director Dynamics

As was stated already in the Introduction, the key quantity controlling the response times for liquid crystal (LC) displays is the rotational viscosity, $\gamma_1$, for the motion of the nematic director. The use of NMR spectroscopy has proven to be particularly attractive for monitoring the field-induced dynamics in LCs as the rotation of the director can readily be observed as a change of the quadrupolar splitting in deuterium NMR spectra [21]. However, complications arise when the director dynamics is fast; due to rapid rotation of the director, the observed quadrupolar splitting changes considerably during the time needed to measure the NMR spectrum, i.e. during the acquisition of the Free Induction Decay (FID) signal. This further leads to observable artefacts in the NMR spectrum.

In the work presented in Papers I and II we developed a theory to describe the artefacts arising from the aforementioned condition. Thus were able to extend the use of deuterium NMR to study fast director rotation. With deuterium NMR experiments and a simulation program written for Gnu Octave and/or Matlab and based on the new theory we studied both the magnetic field and the electric field induced dynamics of the nematic liquid crystal 5CB-$d_2$ (4-pentyl-4‘cyanobiphenyl) specifically deuterated in the $\alpha$-position of the pentyl chain (see Figure 4.1). For the nematogen 5CB the anisotropy of

![Figure 4.1. Nematic liquid crystal 5CB-$d_2$.](image)

the diamagnetic susceptibility tensor, $\Delta \chi$, is positive so that the director aligns parallel to the magnetic field and similarly the anisotropy of the dielectric susceptibility tensor, $\Delta \varepsilon$, is also positive so that the director tends to align parallel to the electric field.

In NMR experiments there is a permanent static magnetic field, but the electric field can be switched on and off to study the field dependence of the director orientation. These
kind of NMR experiments are usually called the turn-on and the turn-off experiments. According to Section 2.2, the effect of competing external electric and magnetic fields on the director can be described with Leslie-Ericksen continuum theory. In general, as in many applications the liquid crystals are confined into small volumes between glass plates, the surface effects and elastic deformations can play a significant role. However, as the practical applications that will be presented in this Chapter deal with relatively large containers resembling a bulk phase and concentrate on the director rotation due to strong external fields, it is assumed that the liquid crystal molecules move as a uniform entity (monodomain) in a bulk phase and, additionally, that the inertial effects are negligible. In this context, we can utilise the simplified torque-balance equation (see Eq. (2.16)), which can now be written as

$$\Gamma_E + \Gamma_M + \Gamma_{\text{vis}} = 0,$$  

(4.1)

If we define $\theta$ to be the angle between the director, $\hat{n}$, and the magnetic field, $B$, and $\alpha$ the angle between $B$ and the electric field, $E$, we can utilise Eq. (2.5) and Eq. (2.8) and write the torques of the external magnetic and electric fields on the director as

$$\Gamma_M = \frac{1}{2 \mu_0} \Delta \chi B^2 \sin(2\theta)$$  

(4.2)

and

$$\Gamma_E = -\frac{1}{2} \varepsilon_0 \Delta \varepsilon E^2 \sin[2(\alpha - \theta)],$$  

(4.3)

respectively. According to Eq. (2.13) the viscous torque for pure rotation is now

$$\Gamma_{\text{vis}} = \gamma_1 \frac{d\theta}{dt},$$  

(4.4)

where $\gamma_1$ is the rotational viscosity coefficient. Now we can write the torque-balance equation (4.1) describing the competing fields as

$$\frac{\Delta \chi}{2 \mu_0} B^2 \sin (2\theta) - \frac{\varepsilon_0 \Delta \varepsilon}{2} E^2 \sin[2(\alpha - \theta)] + \gamma_1 \frac{d\theta}{dt} = 0.$$  

(4.5)

As stated already in Section 2.2, in this approximation a range of other contributions, namely those originating from inertial effects, elastic deformations, flow and surface interactions are neglected. It has been shown [65], that the torque-balance equation, Eq. (4.5), gives the time dependence of the director orientation as

$$\theta(t) = \arctan[\tan(\theta_0 - \theta_\infty) \exp(-t/\tau)] + \theta_\infty,$$  

(4.6)

where $\theta_0$ is the initial angle made by the director with the magnetic field, $\theta_\infty$ is the equilibrium orientation of the director at infinite time after turning the electric field on or off and $\tau$ represents the relevant director relaxation time constant. As in the turn-off experiments only the magnetic field is present, the turn-off director relaxation time, $\tau_{\text{off}}$, can be written straightforwardly as

$$\tau_M = \frac{\gamma_1 \mu_0}{\Delta \chi B^2} = \tau_{\text{off}}.$$  

(4.7)

Under the influence of just the electric field the director relaxation time would be

$$\tau_E = \frac{\gamma_1}{\varepsilon_0 \Delta \varepsilon E^2}.$$  

(4.8)
For the turn-on experiment the orienting forces of the magnetic and the electric field compete and the relaxation time is

$$\tau_{\text{on}} = \gamma_1 \left[ \left( \frac{\Delta \chi B^2}{\mu_0} \right)^2 + 2 \frac{\Delta \chi B^2}{\mu_0} \varepsilon_0 \Delta \varepsilon E^2 \cos (2\alpha) + \left( \varepsilon_0 \Delta \varepsilon E^2 \right)^2 \right]^{-1/2}. \quad (4.9)$$

Since the magnetic field of the spectrometer is fixed, the turn-off relaxation time, $\tau_{\text{off}}$, can only be manipulated by changing the temperature and thus the rotational viscosity of the sample. On the other hand, the relaxation time, $\tau_{\text{on}}$, can also be changed by varying the relative orientation of the two fields and by increasing the electric field thus decreasing $\tau_E$ [23, 65]. As both equations (4.7) and (4.9) contain the rotational viscosity coefficient, $\gamma_1$, experimentally obtained relaxation time constants can be utilised to calculate $\gamma_1$, provided that either $\Delta \varepsilon$ or $\Delta \chi$ is known.

The Hamiltonian operator for the two equivalent deuterons in 5CB-$d_2$ can be written as

$$\hat{H} = \frac{1}{2} \Delta \nu^0_Q P_2 (\cos \theta (t)) \hat{I}_z^2, \quad (4.10)$$

where $\Delta \nu^0_Q$ represents the observable quadrupolar splitting of a static sample (i.e. with the electric field off), and $\theta(t)$ is again the angle between the director and the external magnetic field. The time dependence of the angle $\theta$ arises from the fact that the director rotates during the acquisition of the spectrum. Only the quadrupole coupling is included in the Hamiltonian and all the other interactions are omitted. This is done to simplify the equations to be utilised in developing the theory for the director dynamics and can be easily justified; the Zeeman interaction and the spin-spin coupling constants do not depend on the orientation, the dipolar couplings are small compared to the quadrupolar coupling and were not even resolvable in the experimental data (thus would only slightly change the line widths as the orientation changes), and the anisotropy of the deuterium shielding tensor, that would depend on the orientation, is small enough to be ignored. Utilising the Hamiltonian in Eq. (4.10) together with the spin density matrix theory presented in Chapter 3.4 and including the relaxation effects, the FID signal observed in the turn-on and turn-off experiments can be written as

$$\text{FID} (t + t_0) \propto \cos [\pi \Delta \nu^0_Q f (t + t_0, t_0)] \exp (-t/T^*_2), \quad (4.11)$$

where $T^*_2$ is the effective spin-spin relaxation time constant, $t_0$ is the time delay between switching on/off the electric field and starting the acquisition of the spectrum and

$$f (t + t_0, t_0) = \int_{t_0}^{t+t_0} P_2 (\cos \theta (t')) dt'. \quad (4.12)$$

In a normal NMR experiment for a static sample $f(t) = t$. Inserting Eq. (4.6) for the angle $\theta$ in the integral in Eq. (4.12) and substituting $\theta_0 = 0^\circ$ (turn-on experiment), $f (t + t_0, t_0)$ can be evaluated as

$$f_{\text{on}}(t + t_0, t_0) = P_2 (\cos \theta_\infty) t$$
$$+ \frac{3}{4} \cos (2\theta_\infty) \tau_{\text{on}} \ln [\cos^2 \theta (t_0) + \sin^2 \theta (t_0) \exp (-2t/\tau_{\text{on}})]$$
$$+ \frac{3}{2} \sin (2\theta_\infty) \tau_{\text{on}} \{ \arctan [\tan \theta (t_0) \exp (-t/\tau_{\text{on}})] - \theta (t_0) \} \quad (4.13)$$
If $\theta_\infty = 0^\circ$ (turn-off experiment) the function $f(t)$ reduces to a rather simple form:

$$f_{\text{off}}(t + t_0, t_0) = t + \frac{3}{4} \tau_{\text{off}} \ln[\cos^2(t_0) + \sin^2 \theta(t_0) \exp(-2t/\tau_{\text{off}})] .$$  \hspace{1cm} (4.14)

One of the interesting questions is what are the conditions for the oscillations to be visible in the NMR spectra, i.e., how fast director dynamics is fast enough? Now, the observable quadrupolar splitting, $\Delta \nu_Q$, is

$$\Delta \nu_Q = \Delta \nu_Q^0 P_2(\cos \theta(t)) ,$$  \hspace{1cm} (4.15)

and using Eq. (4.6) for the angle $\theta(t)$ we can write

$$\frac{d\theta(t)}{dt} = -\frac{\sin 2(\theta(t) - \theta_\infty)}{2\tau} .$$  \hspace{1cm} (4.16)

Combining Eqs. (4.15) and (4.16), the rate of change of the quadrupolar splitting can be written as

$$\frac{d\Delta \nu_Q}{dt} = \frac{3\Delta \nu_Q^0}{4\tau} \sin 2\theta(t) \sin 2(\theta(t) - \theta_\infty) .$$  \hspace{1cm} (4.17)

For a turn-off experiment ($\theta_\infty = 0$), Eq. (4.17) reaches a maximum value of

$$\left( \frac{d\Delta \nu_Q}{dt} \right)_{\text{off max}}^{\text{on max}} = \frac{3\Delta \nu_Q^0}{4\tau_{\text{off}}} ,$$  \hspace{1cm} (4.18)

when $\theta(t) = 45^\circ$, and for a turn-on experiment the maximum is reached at $\theta(t) = \theta_\infty/2$ and the maximum rate of change would be

$$\left( \frac{d\Delta \nu_Q}{dt} \right)_{\text{off max}}^{\text{on max}} = \frac{3\Delta \nu_Q^0}{4\tau_{\text{on}}} \sin^2 \theta_\infty .$$  \hspace{1cm} (4.19)

Thus, the rate of change depends not only on the director relaxation time, but also on the 'static' quadrupolar splitting, $\Delta \nu_Q^0$. As the effective spin-spin relaxation time, $T_2^*$, defines for how long the FID signal is observable, it would be reasonable to assume that the relevant question is how much the quadrupolar splitting changes during a time step roughly equivalent to $T_2^*$. At the maximum rate of change the splitting in a turn-off experiment would change by an amount equal to

$$\frac{3\Delta \nu_Q^0}{4\tau_{\text{off}}} \cdot T_2^* .$$  \hspace{1cm} (4.20)

Thus, for a particular sample at a certain temperature ($\Delta \nu_Q^0$ is set), the rate of change of the quadrupolar splitting, and further the visibility of the oscillations, depends on the ratio $\tau/T_2^*$, i.e. how fast is the director relaxation in comparison with the effective spin-spin relaxation rate. It could be further argued, that the change in the quadrupolar splitting could be observable if it changes the splitting sufficiently compared to the spectral line width (Full Width at Half Maximum = $1/(\pi T_2^*)$). In real life, the maximum rate of change for the quadrupolar splitting is only obtained when the director is exactly at a certain angle with respect to the magnetic field. Thus, even if the acquisition of the FID is started with the maximum rate of change the rate would be less than the maximum for some (or even
most) of the time taken to collect the FID. In addition, because of the noise and the line broadening (due to unresolved dipolar splittings, possible deviations of the electric field at different parts of the sample etc.) the oscillations would disappear before reaching the theoretical upper limit of $\tau/T_{2}^{*}$. Anyhow, the above reasoning gives an idea of the relevant parameters effecting the visibility of the oscillations in the NMR spectra.

In the current experiments, the sample was prepared inside a 194.2 $\mu$m thick glass cell that was coated with indium oxide and the cell was inserted into a 7.05 T magnet so that the two fields were approximately orthogonal with respect to each other. The quadrupolar echo sequence was utilised to collect the spectra. The pulse programs and the sample arrangement are illustrated in Figure 4.2.

![Figure 4.2](image.png)

**Figure 4.2.** The pulse sequence for the (a) turn-off and the (b) turn-on experiments and (c) an illustration of the sample.

Eqs. (4.11)-(4.14) were utilised to simulate the deuterium spectrum measured for 5CB-$d_{2}$. An exemplary set of spectra from a turn-off experiment on 5CB-$d_{2}$ and the corresponding simulations are presented in Figure 4.3 and a similar set of spectra from a turn-on experiment in Figure 4.4. The values (ms) in between the experimental and the simulated spectra indicate the delay $t_{0}$ waited before starting to collect a spectrum after turning the electric field off (Figure 4.3) or on (Figure 4.4). As is clear from these pictures, the simulations based on the above equations were able to reproduce the peculiar oscillations observed in the experimental deuterium spectra. In addition, the director relaxation times were obtained directly as fitting parameters from the simulations, and they were found
Figure 4.3. The (a) experimental and the (b) simulated turn-off spectra of the 5CB-$d_2$ measured at $29.5^\circ$C ($\theta_0 = 49^\circ$, $\theta_\infty = 0^\circ$, $B = 7.05$ T).

to be $0.42 \pm 0.01$ ms for the turn-on ($\tau_{on}$) and $0.95 \pm 0.01$ ms for the turn-off ($\tau_{off}$) experiments. The error margins are the maximum difference of the values obtained from simulating different spectra, as each spectrum showing clear oscillations were simulated separately to test the applicability of the theory. In practise, simulating a set of spectra at the same time would naturally lead to more reliable results, but as long as a spectrum with clear oscillations is used, even a single spectrum was shown to give the director relaxation time with good accuracy.

The theory and the simulations were also utilised to explain the differences observed between the current deuterium NMR spectra and the proton NMR spectra measured by Bender et al. for a liquid crystal PCH-5 [25]. It was shown that, even though the theory behind the oscillations observed in both the experiments is fundamentally the same, the different natures of the spin systems lead to different kind of oscillations to be observed in the NMR spectra.

Even though it was stated that it is possible to obtain the director relaxation time constant from a single spectrum, in practice it is also necessary to measure a static spectrum to obtain $\Delta \nu_0^0$. In any case, the instrument time needed to record these two spectra is considerably less than the time needed to measure a series of quadrupolar couplings at different time steps and fitting them to Eq. (4.6), as has been traditionally done. Moreover, in case of fast director dynamics, the quadrupole splitting measured as a difference between the peak tops observed in the spectrum does not match the actual quadrupole splitting that would be observed for a static sample at the same director orientation. Thus, in such cases when the director re-orientation rate is fast enough for the quadrupolar splitting to change considerably during the acquisition of the FID, it was not only found out that the current theory for the director dynamics is able to produce the desired director relaxation
Figure 4.4. The (a) experimental and the (b) simulated turn-on spectra of the 5CB-d$_2$ measured at 30°C ($\theta_0 = 0^\circ$, $\theta_\infty = 82.5^\circ$, $B = 7.05T$, $E = 1.237\text{MVm}^{-1}$).

time constants faster, but that it is a necessary tool to obtain accurate values for these parameters.
5 Magnetic Properties of Small Solute Molecules

In Papers III, IV and V the LC NMR method was extended to study the magnetic properties of small solute molecules. The investigations covered the nuclear shielding, the spin-spin coupling, the dipolar coupling, as well as the quadrupolar coupling tensors. The molecules studied were the series of methyl halides, CH$_3$X ($X = F, Cl, Br or I$), the series of methyl mercury halides, CH$_3$HgX ($X = Cl, Br or I$) and deuterated benzenes. All the LC solvents were uniaxial, thermotropic, and nematic.

In Chapter 3 on the theory of NMR it was seen that the observed anisotropic LC NMR parameters are straightforwardly related to the orientation parameters (See e.g. Eq. (3.15)). Thus they can be used to study the average ordering of molecules. The number of necessary orientation parameters depends on the molecular symmetry. For C$_{3v}$ symmetric molecules, such as CH$_3$X, CH$_3$HgX and 1,3,5-C$_6$D$_3$H$_3$, only one orientation parameter, $S_{zz}$, is needed. In this case the $z$-axis is normally chosen to coincide with the three-fold symmetry axis. On the other hand, to define the orientation of a C$_{2v}$ symmetric molecule, such as C$_6$DH$_5$, two orientation parameters have to be defined. These orientation parameters are usually chosen to be $S_{zz}$ and the difference $(S_{xx} - S_{yy})$. To sample different orientations, $S$ can easily be changed by using different LC solvents or by varying the temperature of the thermotropic LC.

In the current work dipolar couplings were utilised to obtain information about the orientation. Following the procedure described in Section 3.3, the experimentally observable anisotropic coupling, $D_{ij}^{\exp}$, can be divided into following contributions:

$$D_{ij}^{\exp} = D_{ij} + \frac{1}{2} J_{ij}^{\text{aniso}}$$

$$= D_{ij}^e + D_{ij}^h + D_{ij}^a + D_{ij}^d + D_{ij}^c + \frac{1}{2} J_{ij}^{\text{aniso}}$$

(5.1)

(5.2)

where the last term, $J_{ij}^{\text{aniso}}$, is the anisotropy of the spin-spin coupling. As a consequence, either $D_{HH}$ or $D_{CH}$ couplings are a safe choice to be utilised to obtain the orientation parameters, as $J_{ij}^{\text{aniso}}$ has been shown to be negligible for these couplings [66, 67]. The experimental anisotropic coupling, $D_{ij}^{\exp}$, between two magnetically non-equivalent nuclei is tied to the isotropic spin-spin coupling constant; the splitting observed in an NMR spectrum is $\left|2D_{ij}^{\exp} + J_{ij}\right|$. Thus, also the spin-spin coupling constants need to be known. These can be obtained from literature, measured in the isotropic phase of the LC solvent.
or by carrying out Magic Angle Spinning (MAS) experiments to remove the observable anisotropic interactions in the anisotropic phase.

From Eq. (3.37) for the dipolar couplings it is clear, that to be able to calculate the orientation parameter, some information about the molecular geometry – i.e. at least one bond length $r_{ij}$ – needs to be known. On the other hand, for most molecules several dipolar couplings can be measured and thereby information about the relative geometry can be obtained. Moreover, a suitable dipolar coupling can be chosen to be used in the analysis, basing on the accuracy of the available geometric information or the resolution of the measured couplings. It is also possible to use several dipolar couplings to improve the reliability of the orientation parameters and, naturally, more couplings must be used, if more than one orientation parameter is needed to describe the molecular ordering.

The anharmonic and harmonic vibrational contributions to dipolar couplings can be calculated using program AVIBR [58], which also yields an effective $r_\alpha$ geometry (including both the anharmonic contributions and the centrifugal distortions). As an input the program requires a harmonic and an anharmonic force field and the corresponding equilibrium geometry, $r_e$. The treatment of harmonic corrections is implemented also into program MASTER [68], which in addition calculates the solvent induced deformation effects on the experimental dipolar couplings. In this program the user enters the measured dipolar couplings besides the harmonic force field and the corresponding $r_e$ geometry. The bond interaction tensors, $A_{ij}$, introduced in Section 3.3 are further utilised to calculate the orientation parameters by fitting them into rovibrationally corrected experimental data in an iterative procedure. It is also possible to substitute the $r_e$ geometry with an $r_\alpha$ geometry in the iterative process. Thus, instead of using the equilibrium geometry contributions, $D^e$ (cf. Eq. (3.22)), the $r_\alpha$ geometry contributions, $D^\alpha$ (See Eq. (3.34)) to the dipolar couplings are calculated. Consequently, also the anharmonic contributions to the dipolar couplings can be incorporated into the MASTER analysis. Assuming there is enough independent experimental data, refinement of the geometry can be carried out by releasing some of the geometry parameters to be free parameters in the fitting procedure. This would then yield an experimental solution state $r_\alpha$ geometry. All the force fields and the corresponding $r_e$ geometries utilised in the current work were obtained from the literature and the $r_\alpha$ geometries were either from the literature or calculated with the program AVIBR.

It has been observed that the deformation effects on the NMR parameters can be distinguished by using suitable mixtures of liquid crystals, sometimes called the good mixtures [69]. In these mixtures the geometric distortions induced by the solvent molecules are minimised and this is usually demonstrated by vanishing dipolar couplings for the methane molecule in such solvents. For investigations on quadrupolar couplings and electric field gradient tensors, there exists yet another valuable type of mixture, the magic mixture [70]. In these mixtures the EFG produced by the solvent molecules is minimised, so that the EFG experienced by a nuclei arises solely from the electrons and the other nuclei within the molecule. Even if the deformation contributions to the dipolar couplings are calculated with the program MASTER, utilisation of good mixtures has an additional value, as the deformation effects on all the other NMR parameters are supposed to also be small in these mixtures [69]. This is a definitive advantage, as the calculation of the deformation contributions on NMR parameters other than dipolar couplings is not yet implemented into any computer programs.
In Papers III, IV and V, the NMR properties at issue were also studied with \textit{ab initio} (AI) and/or Density Functional Theory (DFT) calculations. If we wish to compare the computational values with the experimental parameters corresponding to a rovibrational average at a finite temperature, \textit{i.e.} parameter $\langle F \rangle^T = F^\alpha + F^h$ is measured, harmonic and anharmonic contributions should be included into the electronic structure calculations. In all three papers on the magnetic properties of small solute molecules, rovibrational corrections were calculated for the experimental dipolar couplings utilised to obtain the orientation parameters, but the calculations of the rovibrational effects on the reported NMR parameters, \textit{i.e.} the nuclear shielding in methyl halides, the spin-spin coupling in methyl mercury halides and the quadrupolar coupling in deuterated benzenes, were incorporated into the computational work. Thus, all the reported results for these parameters represent the corresponding rovibrational average of these properties at a finite temperature, $\langle F \rangle^T$.

### 5.1 Nuclear Shielding in Methyl Halides

![Carbon-13 spectrum of methyl fluoride and methane in an anisotropic phase.](image)

The series of methyl halides (CH$_3$X, X = F, Cl, Br, I) is commonly used as a reference set of molecules in quantum chemical calculations to demonstrate the effect of the halogen atom on the light-atom nuclear magnetic shielding. In spite of that, there had not been any systematic experimental studies on the shielding tensors in methyl halides to provide suitable reference values for the calculations. Previous experimental results were obtained
with versatile methods mostly for only one specific molecule of the series at a time. As a consequence, the results vary over a wide range, especially for the shielding anisotropies. In addition, some of the shielding constants had been measured only in liquid solutions instead of gas phase experiments, that would produce results better suited for comparison with the computational values calculated for isolated molecules.

In Paper III we systematically studied the shielding tensors for $^1\text{H}$ and $^{13}\text{C}$ in the whole series of methyl halides by NMR experiments and state-of-the-art electronic structure calculations. Experimental shielding constants were obtained from a set of gas phase NMR experiments, extrapolating the results to zero pressure limit. LC NMR was used to obtain experimental tensor anisotropies. Methane, $^{13}\text{CH}_4$, was used as an internal reference both in the gas phase experiments and in the LC NMR work to account for the bulk solvent effects. Three different LC solvents were used to obtain information about the possible solvent effects. Deformation effects were covered by using a good mixture as one of the solvents, as well as by utilising the deformation theory implemented in the program MASTER on some of the data. Rovibrational effects were considered both in the experimental dipolar couplings and in the calculated shielding parameters. Computational ab initio (AI) shielding tensors were obtained applying recently developed Breit-Pauli Perturbation Theory (BPPT) to include both the spin-orbit and the scalar relativistic effects on top of the non-relativistic (NR) results. Rovibrational averages were calculated at 300 K to match the experimental conditions (350 K for $\sigma_i(\text{CH}_3\text{II})$).

In case of $C_{3v}$ symmetric molecules, such as the methyl halides, only one orientation parameter, $S_{zz}$, is needed to describe the orientation. The $z$-axis was chosen to be along the $C_X$-bond, i.e. the 3-fold symmetry axis. As all the liquid crystal solvents that were used in this study have a positive anisotropy of the magnetic susceptibility tensor, the term $P_2(\cos \beta) = 1$ in Eq. (3.18) can be dropped out for all the solvents. Combining this with Eqs. (3.19) and (3.20), the chemical shift observed in NMR experiments can be written as

$$\delta_i^{\exp} = \langle \sigma_{\text{ref}} \rangle - \langle \sigma_i \rangle = \delta_i^{\text{iso}} - \frac{2}{3} S_{zz} \Delta \sigma_i,$$

where $\sigma_{\text{ref}}$ is the shielding of the reference molecule, in this case methane, and the shielding anisotropy is expressed with respect to the molecular symmetry axis $z$.

In the current LC NMR work the experimental $D_{\text{HH}}$ couplings were used for calculation of the orientation parameter, $S_{zz}$, and the dipolar couplings were corrected for harmonic and anharmonic vibrations with the program AVIBR, utilising force fields obtained from the literature. The possibly remaining deformation contributions in the solvent MIX (the good mixture) were studied with the program MASTER utilising all the available dipolar couplings: $D_{\text{CH}}$, $D_{\text{HH}}$ – and in case of CH$_3$F; $D_{\text{HF}}$ and $D_{\text{CF}}$ – and the $r_\alpha$ geometries obtained from the analysis with AVIBR. It was concluded that, expectedly, the deformation effects on the $D_{\text{HH}}$ couplings in the good mixture were miniscule and could be safely ignored. The shielding anisotropies were determined with two separate LC NMR methods; namely the Nematic-Isotropic transition method (NI) and the gradient method (GR). In the first method (NI) the isotropic shielding is measured in the isotropic phase and this value alongside the orientation parameter obtained from the dipolar couplings is then used to calculate the anisotropy from Eq. (5.3). In the latter method (GR) the chemical shift in the anisotropic phase is measured with respect to the change of the orientation parameter by changing the temperature. According to Eq. (5.3), a linear fit of this data gives the isotropy as an intercept and the anisotropy as a slope of the fitting curve.
Experimental and calculated $^{13}$C and $^1$H nuclear shielding constants and anisotropies in CH$_3$X ($X = F, Cl, Br, I$) series of molecules.$^a$

<table>
<thead>
<tr>
<th>$X$</th>
<th>AI</th>
<th>Gas</th>
<th>AI</th>
<th>NI</th>
<th>GR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\sigma_C$</td>
<td>$\Delta\sigma_C$</td>
<td>$\sigma_H$</td>
<td>$\Delta\sigma_H$</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>120.3</td>
<td>116.83</td>
<td>103.1</td>
<td>117.2</td>
<td>113.8</td>
</tr>
<tr>
<td>Cl</td>
<td>167.3</td>
<td>163.94</td>
<td>42.5</td>
<td>50.5</td>
<td>49.2</td>
</tr>
<tr>
<td>Br</td>
<td>186.0</td>
<td>182.49</td>
<td>18.3</td>
<td>25.3</td>
<td>20.6</td>
</tr>
<tr>
<td>I</td>
<td>228.4</td>
<td>220.72</td>
<td>-40.8</td>
<td>-34.0</td>
<td>-42.0</td>
</tr>
</tbody>
</table>

$^a$ In ppm. Experimental results are from the gas phase measurements ($\sigma_i$) and from the good mixture ($\Delta\sigma_i$) using the nematic-isotropic transition method (NI) and the gradient method (GR). The experimental chemical shifts with respect to methane were converted into absolute shieldings using $\sigma_C$(CH$_3$I) = 195.1 ppm [71] and $\sigma_H$(CH$_3$I) = 30.61 ppm [72]. Computational $ab$ $initio$ (AI) results are rovibrational averages of the total shielding parameters (NR+BPPT) at 300 K (350 K for $\sigma_i$(CH$_3$I)).

The best experimental and theoretical (AI) results are presented in Table 5.1. The listed experimental results were obtained in solvent MIX. The AI results for the isotropies were found to be in good agreement with the gas phase NMR values as were the calculated anisotropies with the LC NMR results. Especially, the experimental $\Delta\sigma_H$ were surprisingly similar with their computational counterparts, as this parameter is notoriously sensitive to solvent effects, thus extremely hard to obtain reliably.

It was seen that the solvent can have a drastic effect on the values of the anisotropies obtained with LC NMR, as could be predicted on the grounds of the large variation on the previous LC NMR results. The solvent effects were most strikingly present in solvent Phase IV, especially for CH$_3$F, whereas the results using solvent ZLI 1132 were found to be in reasonable agreement with the results obtained in good mixture. In general, it was seen that after choosing a proper solvent and considering the rovibrational effects, LC NMR can give reliable results even for the small proton shielding anisotropies, generally considered to be difficult to obtain accurately. After comparing the experimental results with the computational values and considering the possible sources of uncertainties in the two experimental LC NMR methods (NI and GR), a slight preference was given to the results obtained with the GR method.

With $ab$ $initio$ calculations it was shown that the relativity plays an important role in explaining the nuclear shielding, especially for molecules containing heavier halogens, as the relativistic contributions can account for the bulk of the total value and even determine the sign of the anisotropies. This is clearly visible in Figure 5.2 where the values for the carbon shielding parameters computed at different levels of theory are plotted alongside the experimental results. On the other hand, in this study, the rovibrational averaging was
Figure 5.2. Experimental and computational (non-relativistic (NR) and total (TOT=NR+BPPT)) $^{13}$C nuclear (a) shielding constants and (b) anisotropies in CH$_3$X ($X = F$–I) both at equilibrium geometry ($r_e$) as well as rovibrationally averaged at given temperature. (c) Chemical shifts computed for molecules at the equilibrium geometries. In (d)-(e), errors of the corresponding computational parameters at different levels of theory with respect to the experimental results.

found to be of lesser importance, although excluding these effects would lead to an error of a few percent and should not be ignored if high accuracy is pursued.

Overall, both the experimental and the computational results can be considered to be of reference quality. Especially, as this was the first systematic experimental study on the shielding parameters in the whole series of methyl halides, these results establish a solid foundation for discussions on the relative magnitudes and general trends of the shielding parameters in this series.
5.2 Spin-Spin Coupling in Methyl Mercury Halides

Figure 5.3. Carbon-13 spectrum of methyl mercury chloride and methane in an anisotropic phase. The C-Hg couplings are visible as satellites marked with the stars.

In Paper IV we managed, for the first time, to measure the anisotropies of the $^{199}$Hg−$^{13}$C spin-spin coupling tensors in methyl mercury halides (CH$_3$HgX, X = Cl, Br or I) by LC NMR. These couplings were also produced with Zeroth-Order Relativistic Approximation Density Functional Theory (ZORA DFT) calculations. Due to weak solubility in LC solvents and the small natural abundance of the spin pairs $^{199}$Hg − $^{13}$C, the experimental determination of these parameters is quite tedious. The computations are also demanding as the heavy mercury atom forces to take into account the relativistic effects. These are likely the reasons why there were no previous reports on these spin-spin coupling anisotropies.

As the CHg -bonds are along the three-fold symmetry axis of the $C_{3v}$ symmetric methyl mercury halides, the NMR observable anisotropic part of the $^{199}$Hg−$^{13}$C spin-spin coupling can be written as

$$J_{\text{HgC}}^{\text{aniso}} = \frac{2}{3} \Delta J_{\text{HgC}} S_{zz},$$

(5.4)

where the anisotropy of the coupling tensor is defined as

$$\Delta J_{\text{HgC}} = J_{\text{HgC},zz} - \frac{1}{2} (J_{\text{HgC},xx} + J_{\text{HgC},yy})$$

(5.5)

following the definition given in Eq. (3.13). The z-axis is again chosen to be along the three-fold symmetry axis, i.e. the CHgX -axis. Consequently, Eqs. (5.1) and (5.4) lead to

$$\Delta J_{\text{HgC}} = 3 \frac{D_{\text{exp}} - D_{\text{HgC}}}{S_{zz}}.$$ 

(5.6)
Table 5.2. Experimental and computational $^{13}$C-$^{199}$Hg spin-spin coupling constants and anisotropies of the spin-spin coupling tensors in methyl mercury halides.$^a$

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>MeHgCl</td>
<td>1450</td>
<td>1261.0 (811.7)</td>
<td>1160</td>
<td>1224.4 (1023.9)</td>
<td>0.80</td>
<td>0.97</td>
</tr>
<tr>
<td>MeHgBr</td>
<td>1420</td>
<td>1261.9 (811.6)</td>
<td>1000</td>
<td>1235.9 (1037.7)</td>
<td>0.71</td>
<td>0.98</td>
</tr>
<tr>
<td>MeHgI</td>
<td>1340</td>
<td>1184.3 (757.6)</td>
<td>980</td>
<td>1225.1 (1025.7)</td>
<td>0.73</td>
<td>1.03</td>
</tr>
</tbody>
</table>

$^a$ Computations included 3 DMSO molecules in order to simulate solvent effect. In parenthesis are the corresponding gas phase results.

Thus, the anisotropy of the tensor can be obtained by measuring the corresponding experimental coupling, $D^{\text{exp}}$, calculating the $D$ coupling (including the rovibrational contributions) in a suitable geometry and utilising one of the other dipolar couplings to obtain the orientation parameter, $S_{zz}$.

In Paper IV the $D_{\text{CH}}$ couplings were chosen for the calculation of $S_{zz}$. The experiments were done in a liquid crystal solvent Phase IV. All the dipolar couplings were corrected for harmonic vibrations using the correction coefficients taken from a previous work on CH$_3$HgX. For molecules possessing $C_{3v}$ symmetry this is an acceptable procedure, as the correction coefficients are constants independent of the orientation, thus transferable. The anharmonic vibrations were counted for by using an effective $r_c$, geometry from the literature. The deformation effects were not considered, but within the experimental accuracy, they were concluded to be small. However, the solvent effects were studied to some extent by replicating some of the experiments in another LC solvent, ZLI 1982, and the results were found to be the same within the experimental error limits.

As was explained before, in an NMR spectrum the spin-spin coupling constant is observed in conjunction with the dipolar coupling, thus also the spin-spin couplings had to be determined. Because it was suspected, that the spin-spin couplings might show a significant temperature dependence, a series of experiments at different temperatures in the isotropic phase were performed and the results were extrapolated into the temperature used in the experiments in the anisotropic phase. Indeed, a prominent temperature dependence was observed, especially for the $J_{\text{CHg}}$ coupling constants. Consequently, the extrapolated spin-spin coupling constants led to more accurate results for the dipolar couplings, and thereby the anisotropies of the spin-spin couplings, although the error arising from the extrapolation seemingly deteriorated the precision of the final results.

The final results for the spin-spin coupling tensors both from the LC NMR experiments as well as from the ZORA DFT calculations are listed in Table 5.2. The experimental and the computational results were found to be of the same order of magnitude, but not fully congruent. In addition, the experimental trend, $\Delta J(\text{CH}_3\text{HgCl}) > \Delta J(\text{CH}_3\text{HgBr}) > \Delta J(\text{CH}_3\text{HgI})$, observed also for the spin-spin coupling constants, was not reproduced by the calculations. The reason for the differences was presumed to spring up from solvation, as originally the computational values were obtained for isolated molecules. This was tested with calculations where the methyl mercury halide molecules were surrounded
by a few selected solvent molecules. Indeed, the solvation was observed to have such a significant effect on the anisotropies and the spin-spin coupling constants, that it could explain the observed differences. On the other hand, calculations revealed that the vibrational effects were not able to explain the discrepancy. Thus, it was concluded that the solvent effects were the most feasible explanation for the remaining difference between the experimental and the computational results.

5.3 Quadrupolar Coupling in Deuterated Benzenes

![Proton spectrum of benzene-$d_3$ in an anisotropic phase](image)

Figure 5.4. Proton spectrum of benzene-$d_3$ in an anisotropic phase.

In LC NMR experiments, deuterium quadrupole coupling (DQC) is frequently utilised tool to study the molecular ordering. As the quadrupole interaction also acts as a powerful relaxation mechanism, the quadrupolar couplings are also utilised to obtain information about the dynamics of the molecules. As many organic molecules, particularly liquid crystals, contain phenyl rings, benzene DQC is often used as this tool. Thus, the study on the DQC of benzene, in a sense, brings us back to the theme of the first two papers; the studies on the ordering and the dynamics of the liquid crystals. Due to the frequent use in the studies on orientation and dynamics, there obviously had been several previous studies on this property, but most of the experimental results dated back to the times of older instruments with lower sensitivity and resolution and, for example, the vibrational and the solvent effects were not considered. In addition, as the previous results varied over a range of more than 40 kHz (60 kHz, if the error limits are taken into account) hardly representing an adequate accuracy for further applications, the subject was considered worth revisiting. Also, this was the first attempt to calculate comparable computational results as the rovibrational treatment on the theoretical parameters was conducted for the first time. Thus, in Paper V LC NMR and *ab initio* calculations were used to determine the deuterium quadrupolar coupling constant (DQCC), *i.e.* the element of the quadrupolar
coupling tensor along the CD -bond, in deuterated benzenes.

Due to the \( C_{2v} \) symmetry two orientation parameters are needed for the isotopomer CH\(_3\)D. Thus, the NMR parameters can be expressed using Eq. (3.17) and the observed quadrupolar splitting, \( \Delta \nu_Q \), is

\[ \Delta \nu_Q = \frac{3}{2} \chi_{zz} \left[ S_{zz} + \frac{1}{3} \eta (S_{xx} - S_{yy}) \right], \]

where \( \chi_{zz} \) is the DQCC, as the \( z \)-axis is chosen to be along the CD-bond. The asymmetry parameter of the quadrupole coupling tensor, \( \eta \), is defined according to Eq. (3.14), \( i.e. \)

\[ \eta = \frac{\chi_{xx} - \chi_{yy}}{\chi_{zz}}. \]

The orientation of the \( C_{3v} \) symmetric CH\(_3\)D\(_3\) can be described with just one orientation parameter and the observable splitting becomes

\[ \Delta \nu_Q = \frac{3}{2} \chi_{zz} S_{zz} (1 + \eta). \]

In Eq. (5.9) the \( z \)-axis is exceptionally chosen to be along the CD-bond instead of the three-fold symmetry axis to retain the naming of the quadrupolar coupling and the orientation tensor elements consistent with Eqs. (5.7) - (5.8).

The measured experimental \( D_{HH}, D_{HD}, D_{DD} \) and one-bond \( D_{CH} \) couplings were corrected for harmonic vibrations and deformation effects with the program MASTER and the anharmonic vibrations were taken into account by utilising \( r_\alpha \)-geometry. The isotropic spin-spin couplings were adopted from the literature. The experiments were carried out using several LC solvents, including the so-called good and magic mixtures, to observe possible solvent effects. In addition, several different temperatures were sampled to study the temperature dependence of the DQCC. As there is one splitting and two unknown parameters in both Eqs. (5.7) and (5.9), \( i.e. \) there is not enough information on the LC NMR data to obtain both the DQCC and the asymmetry parameter experimentally, the asymmetry parameter needed for the experimental analysis was adopted (a) from the literature or (b) from the current calculations.

The experimental LC NMR and the computational AI results obtained in Paper V are represented in Table 5.3. Based on both the experiments and the calculations, the quadrupole coupling tensor seemed to be insensitive to the isotopic substitutions. Thus, in principle, it should be possible to combine the experimental data for the different isotopomers and to fit it to Eqs. (5.7) and (5.9) to obtain experimental information also about the asymmetry parameter besides the DQCC. In practice this appeared to be an unattainable goal, as the small absolute value of \( \eta \) makes fitting it to the experimental data intolerable to even the smallest uncertainties on the magnitude of the experimental couplings and thereby on the values of the orientation parameters. In the experimental temperature series no notable temperature dependence was observed.

Although the experimental and the computational results were in good agreement, there existed a slight difference as the computational value exceeded the experimental value by ca 2 to 4 kHz. As the solvent effects were thought to be a possible culprit again, the solvation was studied computationally using a self-consistent reaction field (SCRF) model, \( i.e. \) placing the molecule into a dielectric continuum describing the solvent. Based

\[ ^1 \text{Note: in Paper V the quadrupolar splitting is denoted as } 2B \equiv \Delta \nu_Q \]
Table 5.3. Deuterium quadrupole coupling constant in deuterated benzenes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>DQCC (kHz)</th>
<th>η</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅D</td>
<td>LC NMR</td>
<td>187.7±0.4⁺</td>
<td>0.041ᵇ</td>
</tr>
<tr>
<td>1,3,5–C₆H₃D₃</td>
<td>LC NMR</td>
<td>187.3±0.3⁹</td>
<td>0.041ᵇ</td>
</tr>
<tr>
<td>C₆D₅</td>
<td>LC NMR</td>
<td>185.0±0.4⁸</td>
<td>0.056ᶜ</td>
</tr>
<tr>
<td>1,3,5–C₆H₃D₃</td>
<td>LC NMR</td>
<td>184.7±0.3⁸</td>
<td>0.056ᶜ</td>
</tr>
<tr>
<td>C₆H₅D</td>
<td>ab initio (MP2)ᵈ</td>
<td>189.54</td>
<td>0.0557</td>
</tr>
<tr>
<td>1,3,5–C₆H₃D₃</td>
<td>ab initio (MP2)ᵈ</td>
<td>189.63</td>
<td>0.0564</td>
</tr>
<tr>
<td>C₆D₁₀</td>
<td>ab initio (MP2)ᵈ</td>
<td>189.44</td>
<td>0.0555</td>
</tr>
</tbody>
</table>

² Error margin from one standard deviation of the results obtained in different LC solvents.
ᵇ η from Ref. [73].
ᶜ η from the current calculations.
ᵈ MP2 calculations including rovibrational corrections at 300 K (see Paper V for more details).

on these calculations, it could be deduced that the long range electrostatic interactions between the solvent and the solute molecules could not explain the difference. This does not exclude the possibility of specific, short range solute-solvent interactions, but as these were partly treated by using several LC solvents and utilising the deformation theory, it is unlikely that they would give rise to a difference of 2 kHz. As can be seen from the experimental result on Table 5.3, the choice between the two different values for the asymmetry parameter produced a difference of ca 2 kHz in the end results. It is also worth to emphasise, that the rovibrational effects were found to be important as, for example, ignoring these effects on the calculations, instead of the current margin of 2 kHz there would be a 12 kHz difference between the experimental and the computational results. However, in both the experimental analysis and in the calculations, the most influential property was found to be the chosen geometry; as can be seen from Figure 5.5, the CD-bond length has a major effect on the experimental results (−0.5 kHz / 0.001 Å) and even more pronouncedly on the theoretical results (−1.1 kHz / 0.001 Å). Thus, the ambiguity of the underlying geometrical parameters, especially the r₃D bond length, was concluded to be the likely source of the remaining difference between the experimental and the computational results, although the specific solvent effects and the unclarity on the right value for the asymmetry parameter could not be totally ruled out as being part of the problem. In any case, we were able to substantially narrow down the wide spread of experimental values for the benzene DQCC, and the current experimental result was verified by state-of-the-art theoretical computations.
Figure 5.5. The effect of the choice of the $r_{CD}$ bond length on (a) experimental and (b) computational DQCC in $C_6H_5D$. The dashed line in plot (a) represents the $r_{CD}$ bond length used in the experimental analysis.
6 Conclusions

The main theme of the present thesis has been the liquid crystal NMR spectroscopy and this versatile method has been utilised to study the dynamics of the LC director as well as the magnetic properties of small solute molecules in liquid crystalline solvents.

Nowadays one of the main objectives of the applications of liquid crystals is to develop faster and faster LC displays, which also creates demand for methods to experimentally study such fast orientation processes. In the present work a new theory was developed to describe the experimentally observable oscillations in the NMR spectra when studying the liquid crystal director dynamics (Papers I and II) under the influence of external fields. A specifically deuterated liquid crystal molecule 5CB-$d_2$ was chosen as a test system and a series of deuterium spectra were recorded. The deuterium NMR combined with spectral simulations based on the new theory was shown to be a valuable method to obtain information about the dynamics in the limit of fast director rotation, where the conventional NMR methods fail. In addition, this new method makes it possible to obtain this information with much less experimental effort as, in principle, it is possible to extract an accurate director relaxation time from a single spectrum instead of a series of spectra.

The other line of study presented in this thesis was the utilisation of liquid crystals as solvents to study other molecules (Papers III, IV and V). Due to narrow spectral lines – hence well resolved spectra – the LC NMR has a capability to provide highly accurate anisotropic nuclear magnetic parameters. However, as has been noted several times both in the summary and in the corresponding papers, there are a few possible pitfalls in the LC NMR method that can lead to skewed results. The vibrational effects and solute-solvent interactions have been discussed extensively in this thesis and are to be thoroughly considered. Furthermore, a good knowledge of a proper geometry of the molecule is in need. Despite of how many experimental parameters are available for the fitting procedure, at least one molecular geometric parameter needs to be know for the analysis of the dipolar couplings. That is why there always lies a slight ambiguity on the final results, but by using a reliable (experimental and/or computational) $r_\alpha$, geometry one can minimise this uncertainty as the only ambiguity left is the effect of solvation on the molecular geometry. Even this can be taken into account to some extent, provided there is enough independent experimental data so that some of the geometric parameters can also be fitted during the iterative analysis of the data.

Traditionally, the experiments have provided reference values for the theoretical work.
Because of the development of computational theories and computer power, the state-of-the-art computations can nowadays provide reliable, self-sufficient data to give invaluable insight into the distinct interactions summing up to observable NMR parameters. Consequently, the calculations can help with the interpretation of experimental spectra as well as with the evaluation of the reliability of experimental methods. In the future, as the computational methods further develop to enable simulations of truly realistic experimental conditions, such as the solvent interactions in liquid crystalline environments, we might be able to combine the experimental and the computational data in our aim to better understand the solute-solvent interactions.

The knowledge of the temperature dependence of the NMR parameters, as well as of the isotropic parameters needed for the analysis, can be important while analysing the experimental LC NMR data. Depending on the LC solvent and the system under study, all the parameters (spin-spin couplings, shielding isotropies, shielding anisotropies, and quadrupolar couplings) can be highly dependent on the temperature. There is also a possibility of an abrupt change in the isotropic parameters when going from an isotropic to an anisotropic phase. In the present studies the uncertainty of the temperature dependence and/or the behaviour in the phase transition was found to be somewhat problematic in the work on the spin-spin couplings ($J_{CH}$ in CH$_3$HgX) as well as with the isotropies and the anisotropies of the shielding tensors (CH$_2$X). These problems might be alleviated by utilising a new method introduced recently by Tallavaara and Jokisaari [74]. In their work they introduced a brilliant idea of utilising porous material dissolved into the liquid crystal to create an environment where both the isotropic and the anisotropic phase can be found simultaneously, thus enabling determination of all the parameters at the same temperature. The natural downside of introducing yet another complex media, the porous material, into the system, is that it is likely to complicate the problem of dealing with the solute-solvent interactions, and also generally seems to worsen the spectral resolution by increasing the line-widths. In addition, the same problems with choosing a proper LC solvent to minimise the local solvent effects persist with this method. However, further experiments and developments of this ingenious idea of how to determine the isotropic parameters alongside the anisotropic parameters will hopefully clarify the effect of the temperature and the phase transitions on the experimental NMR parameters.

Despite of all the effort to point out all the possible pitfalls of the method, during this work the LC NMR was demonstrated to be a feasible tool to obtain accurate reference values for the magnetic properties of small solute molecules, as long as care is taken to consider the possible contributions arising from the molecular movements and the solute-solvent interactions. After considering these effects, both in the analysis of the experimental data and in the computational work, a good compatibility was found between the LC NMR results and the state-of-the-art ab initio calculations of the corresponding parameters for the $^1$H and $^{13}$C shielding tensors in methyl halides, for the anisotropies of the C-Hg spin-spin coupling tensors in methyl mercury halides and for the deuterium quadrupole coupling constant in deuterated benzenes.

As a summary it could be stated, that, once again, the liquid crystal NMR spectroscopy proved to be an extremely versatile and extensive tool to obtain information not only about the complex LC materials themselves, but also about the NMR properties of solute molecules.
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Original papers


