Doctoral Thesis

CPW microresonators for EPR spectroscopy and some advances in solid-state nuclear magnetic resonance

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CPW Microresonators for EPR Spectroscopy and Some Advances in Solid-State Nuclear Magnetic Resonance

A dissertation submitted to
ETH Zurich
for the degree of
Doctor of Sciences

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2010
# Contents

<table>
<thead>
<tr>
<th>Contents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acknowledgments</td>
</tr>
<tr>
<td>Abstract</td>
</tr>
<tr>
<td>Zusammenfassung</td>
</tr>
</tbody>
</table>

## 1. Microresonator for EPR spectroscopy

1.1. Introduction .................................. 15
1.2. Spin Sensitivity of a Microcoil Sensor .......... 17
1.3. Model ........................................ 18
   1.3.1. Model Assumptions ....................... 18
   1.3.2. Maxwell Equations ....................... 19
   1.3.3. Potentials ................................ 21
   1.3.4. Mixed Potential Integral Equation .......... 21
   1.3.5. Spectral Domain .......................... 23
   1.3.6. Green’s Functions ....................... 25
   1.3.7. Method of Moment ......................... 28
   1.3.8. Implementation ......................... 33
1.4. Results ..................................... 37
   1.4.1. Open λ/2 resonator ....................... 38
   1.4.2. Short-circuited λ/4 resonator ............. 43
1.5. CST Microwave Studio Simulations ................ 47
1.6. Summary ..................................... 50
1.7. Conclusion ................................... 50
2. Decoupling during TOBSY Sequences

2.1. Introduction

2.2. Spin Hamiltonian

2.2.1. Chemical-Shift Hamiltonian

2.2.2. J-Coupling Hamiltonian

2.2.3. Dipolar-Coupling Hamiltonian

2.2.4. Rf Hamiltonian

2.2.5. Frame Transformations

2.2.6. Liouville - von Neumann Equation

2.3. C/R Theory

2.4. TOBSY Pulse Sequence

2.5. Parameters used in Numerical Simulations

2.6. Improving Polarization Transfer with an SC9 Sequence

2.6.1. Experiment

2.6.2. Results

2.7. XiX-decoupling during PC9

2.7.1. Experiment

2.7.2. Results

2.7.3. Conclusion

2.8. Generalisation of XiX to Dual-Channel Symmetry-based Sequences PC9\textsubscript{CN}\textsubscript{6}

2.8.1. C-Sequences Decoupling without z-Rotation

2.8.2. C-Sequences Decoupling with z-Rotation

2.8.3. L-Sequences Decoupling with z-Rotation

2.9. Conclusion

2.10. Outlook

3. Dipole-Compensated Adiabatic Pulses

3.1. Introduction

3.2. Theoretical Derivation
<table>
<thead>
<tr>
<th>Section</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3. Adiabatic Pulses</td>
</tr>
<tr>
<td>3.3.1. Hyperbolic Secant Pulses: \textit{sech}</td>
</tr>
<tr>
<td>3.3.2. WURST Pulses</td>
</tr>
<tr>
<td>3.3.3. Compensated Pulse With Piecewise-linear Function $\theta(t)$: \textit{complin}</td>
</tr>
<tr>
<td>3.3.4. Compensated Pulse With a Smoother Function $\theta(t)$: \textit{compsech}</td>
</tr>
<tr>
<td>3.3.5. Adiabaticity Factors $Q(t)$</td>
</tr>
<tr>
<td>3.3.6. Averaging out Homonuclear Dipolar Couplings</td>
</tr>
<tr>
<td>3.4. GAMMA Simulations</td>
</tr>
<tr>
<td>3.5. Use of Dipole-compensated Pulses as C-Element in TOBSY sequences</td>
</tr>
<tr>
<td>3.6. Conclusion</td>
</tr>
<tr>
<td>3.7. Outlook</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Section</th>
</tr>
</thead>
<tbody>
<tr>
<td>4. Conclusion</td>
</tr>
<tr>
<td>5. Outlook</td>
</tr>
<tr>
<td>A. Derivation of the Potentials for coplanar configuration (CPW)</td>
</tr>
<tr>
<td>Bibliography</td>
</tr>
</tbody>
</table>
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Abstract

This thesis is subdivided into three parts. This first part was carried out under the supervision of Prof. Arthur Schweiger († 2006) and Dr. Giovanni Boero (EPFL). The last two parts have been completed in the solid state nuclear magnetic resonance group headed by Prof. Beat Meier.

The first part, comprising Chapter 1, deals with different types of microresonators to be used at X-Band (10 GHz) for electron spin resonance (ESR). The microresonators are based on coplanar technology (CPW) and contain a microcoil whose center is the sample position. We study numerically the magnetic field generated by the microcoil using the mixed-potential integral equation technique (MPIE). We solve the integral equation using the standard Moment Method, where the integral equation is transformed into a linear system for the unknown expansion coefficients of the surface current. The main asset of this approach compared to standard finite-difference time domain (FDTD) or finite-element (FEM), is that the translational and rotational symmetries of Green’s functions for stratified media can be used to full advantage. If the working frequency is kept fixed (here at 10 GHz), all Green’s functions, which contain the full information about the stratified medium, can be precomputed and interpolated as a function of the source-observer distance, thus reducing considerably the amount of computational power. Moreover, the use of a special mapping scheme based on the symmetry of the basis- and test-functions used to solve the MPIE, permits one to compute and store solely the non-redundant matrix-terms. The full Moment Matrix is computed only once at the beginning of the matching/tuning process. During all subsequent runs, only the Matrix-Element corresponding to the surface current cells at the extremities of the resonator (thus changing its length) or around the matching gaps must be recomputed. This allows one to speed up considerably the optimisation process. We were thus able to gain a time-saving factor up to 50 compared to CST Microwave Studio.

In Section 1.2 we recall on which parameters depends the spin sensitivity of an ESR microcoil.
sensor. **Section 1.3** gives the theory behind the MPIE model. We study here two types of resonators, namely $\lambda/2$-open-ended and $\lambda/4$-shorted resonators and vary parameters such as the microcoil diameter and the microcoil gap before computing the normal magnetic field generated by the structure. Each resonator is numerically matched and tuned by varying a matching gap (or two in the case of opened-$\lambda/2$-resonators) and its length respectively. **Section 1.4** contains the simulated normal magnetic field intensities along with the surface current generated on the different structures.

Surprisingly, for the three loop diameters $d$ tested (100 $\mu$m, 200 $\mu$m and 300 $\mu$m), we do not find the maximum magnetic field intensity for the smallest loop (100 $\mu$m) neither for $\lambda/2$-open-ended nor for $\lambda/4$-shorted resonators. This may be due to the influence on the ground plane on the magnetic field for increasing loop diameters, this effect being absent for microstrip configurations. For a given loop diameter and a given source power, the maximum of the magnetic field intensity is about the same order of magnitude for both types (although a little less for the $\lambda/4$-shorted). We conclude that both resonator-types are valid candidates for ESR-spectroscopy.

The second part concerns the proton decoupling during rotor-synchronised symmetry-based pulse sequences in solid-state nuclear magnetic resonance (C/R sequences). Symmetry-based pulse sequences are an elegant way to tailor effective Hamiltonians containing only specific interactions using Average Hamiltonian Theory (AHT). The selection is done via interferences between the space- and spin-rotations, which lead to symmetry selection rules for the different interactions depending on their spin- and space-rank. The space rotation is the sample rotation under magic-angle spinning, while the spin rotation is generated via the pulse sequence. Those sequences are constructed by concatenation of $N$ basic elements (C- or R-element) each phase-shifted by $\frac{2\pi
u}{N}$ with respect to the previous one and spanning $n$ rotor periods. According to which basic element is used (C- or R-element), the sequence is called, $CN_n^\nu$ or $RN_n^\nu$ respectively. Here, we use solely C-sequences with as basic C-elements, POST-elements ($\pi/2$)$^0\nu$($2\pi$)$^{180\nu}$($3\pi/2$)$^0\nu$. Such sequences are labeled $PCN_n^\nu$.

This work is mainly concerned with the heteronuclear decoupling during isotropic homonuclear transfer C-sequences, also called Total Through Bond Spectroscopy (TOBSY). Indeed, when deriving the selection rules for homonuclear sequences, a perfect heteronuclear decon-
pling is assumed, condition not necessarily fulfilled experimentally. We study the transferred magnetization from a first $^{13}$C spin to a second in a two-spin system ($2,3$-$^{13}$C-sodium propionate or $1,2$-$^{13}$C-$^{15}$N-glycinethylester) under $^1$H-decoupling. In Section 2.6 we demonstrate a supercycled-version PSC$^9_{16}$ of the PC$^9_{16}$ sequence under CW proton decoupling leading to an enhanced polarization transfer, the supercycle being defined as $SC_n^\nu = C_n^\nu C_n^{-\nu}$.

In Section 2.7 we study extensively an XiX-decoupling (or series of pulses of length $\tau_{p,XiX}$ and intensity $\nu_{XiX}$, one pulse being $\pi$-phase-shifted with respect to the previous one) on the proton channel while applying a TOBSY sequence on the carbon channel. For a fixed MAS-frequency $\nu_r$, we screen the XiX-modulation frequency $\nu_{m,XiX}$ and decoupling field intensity $\nu_1$, and observe the transferred polarization. Compared to CW-decoupling, we find two specific modulation frequencies $\nu_{XiX}$ with a higher polarization transfer. Those modulation frequencies are $\nu_{m,XiX} = \nu_r$ and $\nu_{m,XiX} = \nu_1$.S.

In Section 2.8 we generalise the condition $\nu_{m,XiX} = \nu_1,S$ by noting that it can be written as a dual channel C-sequence PC$^9_{16}$LiL$18^{0}_{6}$ or PC$^9_{16}$L$36^{18}_{6}$ with L a rectangular pulse with arbitrary flip angle and LiL the concatenation of two such pulses, the second $\pi$-phase-shifted with respect to the first one. We first derive, using the Mathematica package of Levitt, 185 sequences with z-rotation PC$^9_{16}$CN$^\nu_{6}$ as well as 10 sequences PC$^9_{16}$CN$^{0}_{6}$ without z-rotation (meaning $\nu=0$) leading to a scalar average Hamiltonian with the minimum numbers of terms. The derived sequences are then tested numerically using the GAMMA package. We found the interesting sequences PC$^9_{16}$L$36^{17}_{6}$ and its minus-$\nu$ counterpart PC$^9_{16}$L$36^{19}_{6}$ which appear very promising.

Finally, the third part introduces new adiabatic inversion pulses with the property of refocussing the homonuclear dipolar evolution in a nonequilibrium polarization state. Those pulses generate, under specific conditions, two polarization echoes in the effective field which is characterized by its intensity $\nu_{eff}$ und its angle $\theta$ from the $+z$-axis. The first echo is formed when the effective field is aligned along the transverse plane of the Bloch sphere and the second one is formed in the end of the inversion (after the inversion time $t_{inv}$, when the effective field lies along the -$z$-axis, antiparallel to its starting position. In the effective field, the homonuclear scalar interaction scales with the second-order Legendre polynomial $P_2(\cos \theta)$ where it changes sign.

10
at the magic angles $\theta_m$ and $\pi - \theta_m$. The key point is to shape the function $\theta(t)$ which is time-dependant for adiabatic sweeps such as to obtain the condition $\int_0^{t_{inv}} P_2(\cos \theta(t))\,dt = 0$, or in other words, such that the time-average of the scaling factor of the dipolar interactions over the inversion time $t_{inv}$ vanishes. We call this process of shaping the function $\theta(t)$ to average out specific interactions *theta averaging*. We propose two kind of compensated pulses, *complin* where the function $\theta(t)$ is piecewise-linear, and *compsech* with a smoother shape for $\theta(t)$ and better adiabatic properties. To check the new concept, we inspect numerically the non-equilibrium magnetization inversion of the two newly proposed pulses and compare them with the standard inversion pulses: *sech* and *WURST*. Finally, we successfully implement the *complin* pulse in the TOBSY sequence (*complin)*i(*complin)*924 and demonstrate a 10% improved experimental polarization transfer obtained on a 2,3-$^{13}$C-sodium propionate sample compared with the WiW924 sequence, based on *WURST* pulses.
Zusammenfassung


Der erste Teil entstand innerhalb der ehemaligen Forschungsgruppe von Professor Arthur Schweiger (EPR). Er wurde durch Professor Arthur Schweiger sowie Dr. Giovanni Boero von der EPFL betreut.

Der zweite sowie der dritte Teil entstanden innerhalb der Forschungsgruppe von Professor Beat H. Meier (Festkörper-Kernmagnetische Resonanzspektroskopie/Solid-state Nuclear Magnetic Resonance), betreut von Professor Beat H. Meier.

den Matrixelemente erneut berechnet. In dieser Arbeit werden $\lambda/2$-open-ended und $\lambda/4$-shorted Resonatoren und deren Spulendurchmesser sowie der Spulenabstand untersucht. Für die drei simulierten Spulendurchmesser $d$ (100 $\mu$m, 200 $\mu$m und 300 $\mu$m) wird die maximale Intensität des magnetischen Feldes für einen Durchmesser von 200 $\mu$m gefunden. Ein möglicher Grund hierfür wäre der Einfluss der Massefläche auf das Feld in der Spule. Für konstant gehaltene Durchmesser weisen beide Resonatorarten eine H-Feldintensität derselben Grössenordnung auf. Daraus wird geschlossen, dass beide Resonatorarten gültige Kandidaten zur ESR-Spektroskopie sind.

In Kapitel 2 wird die heteronukleare Entkopplung mit rotorsynchronen, symmetriebasierenden Pulssequenzen (C/R Sequenzen) untersucht. Symmetriebasierende Sequenzen erlauben die Herstellung mittlerer Hamiltonoperatoren, die nur spezifische Wechselwirkungen enthalten. Die Selektion wird durch Real- und Spin-Raum-Interferenzen durchgeführt. Dieser Teil der Dissertation befasst sich mit der heteronuklearen Entkopplung während isotropischer, homonuklearer Transfer C-Sequenzen. Dabei wird der Transfer der Polarisierung von einem ersten $^{13}$C Spin nach einem zweiten in einem zwei-Spins-System ($^{2,3}$-$^{13}$C-Natriumpropionat oder $^{1,2}$-$^{13}$C-$^{15}$N-Glycin ethyl ester) unter $^1$H-Entkopplung untersucht. Eine superzyklische Version PSC9$_6^1$ erlaubt einen 10 % erhöhten Polarisationstransfer im Vergleich zu PC9$_6^1$. Danach wird der Effekt der Modulationsfrequenz der XiX-Entkopplung $\nu_{m,\text{XiX}}$ auf den Magnetisierungstransfer extensiv analysiert. Zwei gute Bedingungen wurden im Rahmen dieser Arbeit gefunden: $\nu_{m,\text{XiX}} = \nu_t$ und $\nu_{m,\text{XiX}} = \nu_{1,S}$. Schliesslich wird die gute Bedingung $\nu_{m,\text{XiX}} = \nu_{1,S}$ anhand der C-Theorie für zwei Kanäle verallgemeinert.

In Kapitel 3 werden neue adiabatische Invertierungspulse eingeführt, welche homonukleare, dipolare Kopplungen total oder partiell unterdrücken können. Ein Puls erzeugt zwei Polarisationsechos. Das erste in der Mitte des Pulses, wenn das effektive Feld in der xy-Ebene steht; das zweite am Ende der Invertierung, wenn das effektive Feld entlang der -z-Achse der Blochsphäre steht. Die Pulse werden durch die Intensität $\nu_{\text{eff}}(t)$ vom effektiven Feld und dem Winkel $\theta(t)$ von der +z-Achse charakterisiert. Im effektiven Feld skaliert eine homonukleare, dipolare Wechselwirkung als Legendre-Polynom zweiter Ordnung $P_2(\cos \theta)$. Die Wechselwirkung verschwindet, wenn der Winkel $\theta(t)$ dem magischen Winkel $\theta_m$ gleich. Der Stichpunkt ist die zeitabhängige Funktion
\(\theta(t)\) so zu wählen, dass die Bedingung \(\int_0^{t_{\text{inv}}} P_2(\cos \theta(t)) \, dt = 0\) erfüllt wird. Vorgeschlagen werden zwei Arten von kompensierten Pulsen: *Complin* mit einer stückweise linear Funktion \(\theta(t)\) sowie *compsech* mit einer glatteren Funktion \(\theta(t)\), und daher ein besseres adiabatisches Verhalten. Um das Konzept zu bestätigen, wurde die Invertierung der Nichtgleichgewicht-Polarisation simuliert. Die Ergebnisse wurden auch mit den standard *sech*- und *WURST*-Pulsen verglichen. Schliesslich wurde der *complin* Puls als C-Element in der TOBSY-Sequenz (*complin*)\(i\)(*complin*)\(9_{\text{complin}}\) implementiert und auf 2,3-\(^{13}\)C-Natriumpropionat experimentell getestet. Ein 10 % erhöhter Polarisationstransfer im Vergleich zu WiW\(9_{\text{complin}}\) wurde dabei beobachtet.
1. Microresonator for EPR spectroscopy

1.1. Introduction

Microresonators are an attractive alternative to standard cavities for signal detection of micrometric samples in electron paramagnetic resonance (EPR)\footnote{named after its inventor C.P. Wen \cite{wen}}. Among the many possibilities of transmission line resonators at microwave frequencies \footnote{\cite{wech}} we can cite microstrip resonators, CPW (coplanar waveguide) resonators, slot lines resonators or CPW-grounded resonators. Moreover, we can then choose between a $\lambda/2$ open-circuited or a $\lambda/4$ short-circuited resonator\footnote{\cite{wech}}.

Recently Narcowicz et al. \cite{3} demonstrated two different microstrip resonators working at 14 GHz and their corresponding application for EPR spectroscopy. In this work, we use coplanar technology (CPW\footnote{\cite{1}}) at X-Band (10 GHz). One of the asset of CPW technology compared to microstrip technology is that only one side of the dielectric substrate needs to be copper electroplated.

In Section 1.2 we first recall the different factors affecting the spin sensitivity of a microcoil sensor. This latter is proportional to the magnetic field generated at the sample position for a given source power. This basically means that for a tuned and matched resonator at the desired operating frequency (here 10 GHz) this quantity has to be maximized.

The aim of this work is to study numerically different resonators to find the one with the highest magnetic field intensity at the sample position for a given source power. Here we study different $\lambda/2$ opened and $\lambda/4$ shorted microcoil resonators by varying the microcoil loop diameter and the microcoil gap thickness. The resonators are matched to a 50 $\Omega$ CPW-transmission line through a capacitive gap. For a given geometry, the resonators should be matched and tuned at 10 GHz (X-Band) by varying the capacitive gap and the resonator length respectively.
The strategy chosen is the Mixed Potential Integral Equation (or MPIE\cite{5}) where only the conductor needs to be discretized, as compared with standard techniques such as Finite-Difference Time Domain (FDTD) which is computationally more demanding. Furthermore, in addition to the surface current $J_s$, the MPIE takes directly the induced surface charged density $q_s$ into account.

The integral equation is then solved using the Method of Moment (MoM)\cite{6}. In this approach, we expand the surface current using a set of basis functions and test the required boundary condition using another set of test functions. The Integral Equation is then transformed into a linear system which can be solved for the unknown coefficients of the surface current expansion.

The main advantage of the MoM scheme is that the numerical computations can be considerably speeded up compared to FDTD schemes for three reasons. First, we work at a fixed frequency $f_0=10$ GHz and change the size of the structure to find resonance. This means that for a given substrate height $h$ and dielectric constant $\epsilon_r$, the Green’s functions are computed once only. They are then stored and retrieved with a cubic-spline interpolation scheme. Second, the whole content of the matrix, which contains many redundant elements, can be stored in a compact form using a special mapping scheme\cite{7}. Third, when matching and tuning the structures, the whole MoM matrix needs to be computed once only at the beginning. For all subsequent runs, where the resonator lengths and matching gaps are screened, we need to recompute only the elements of the Moment Matrix corresponding to surface current cells at the edge of the resonators and around the gap respectively. The time gained with this strategy is considerable compared to standard FDTD softwares which are extremely time-consuming for optimization purposes.

Originally, the MPIE in \cite{5} was developed for microstrip structures (with an open half-space above the dielectric substrate and a ground plane below). The MPIE is still valid for CPW-structures provided the Green’s functions for the scalar and vector potentials are rederived using the correct boundary condition (open half-spaces below and above the substrate) (see Appendix A).
1.2 Spin Sensitivity of a Microcoil Sensor

In this section we derive the spin sensitivity as in [1]. Using the reciprocity principle [8], the ESR signal $S(t)$ (in V) can be written [1]:

$$S(t) = - \int \frac{d}{dt} [B_u(r) \cdot M(t, r)] dV_s$$

(1.1)

where $B_u(r)$ is the magnetic field (in T/A) at position $r$ produced by a unitary direct current (dc) carried by the microcoil (also called unitary field), $M(t, r)$ is the spin magnetization (in A/m) at position $r$, and $V_s$ is the sample volume (in m$^3$). By assuming a homogeneous unitary field $B_u(r)$ inside the microcoil sensitive volume $V_s \sim (1/4) d^3$ (with $d$ the microcoil diameter) and zero elsewhere, under quasisteady-state condition [9, 10] and far from saturation, the maximum of the absorption signal can be written

$$S_{\text{max}} \cong (\gamma B_1 M_0) \left( \frac{B_0}{\Delta B} \right) B_u V_s$$

(1.2)

with $B_1$ the applied radio-frequency (rf) magnetic field (in T), $\Delta B$ the half width at half maximum of the resonance line (in T), $N$ the spin density (in m$^{-3}$), $B_0$ the applied static magnetic field (in T), and $T$ the sample (and microcoil) temperature (in K) and where the static magnetization $M_0$ (in A/m) for a spin 1/2 system with $g=2$ is given by

$$M_0 = \frac{1}{4} N \gamma^2 \hbar^2 k T B_0$$

(1.3)

Assuming that the noise stems only from the microcoil series resistance $R$, the signal-to-noise ratio can be defined as:

$$\text{SNR} = \frac{S_{\text{max}}}{3 N_{\text{rms}}} \cong \frac{(\gamma B_1 M_0) \left( \frac{B_0}{\Delta B} \right) B_u V_s}{3 \sqrt{4 k T R \Delta f}}$$

(1.4)

where $\Delta f$ is the equivalent noise bandwidth of the detection electronics and the factor 3 has been added as in [1]. The spin sensitivity (in spins/Hz$^{1/2}$), which tells the minimum number of detectable spins for a frequency bandwidth of 1 Hz, can be defined as:

$$N_{\text{min}} = \frac{1}{\text{SNR}} \frac{N V}{\sqrt{\Delta f}} = \alpha \frac{T^{3/2} \sqrt{R} \Delta B}{B_u B_0^3 B_1},$$

(1.5)

with $\alpha = 24 k^{3/2} \gamma^{-3} \hbar^{-2} \mathrm{kg}^{5/2} \mathrm{s}^{-4} \mathrm{K}^{-3/2} \mathrm{A}^{-3}$.

For homogeneously broadened lines with relaxation times $T_1 \cong T_2$, $B_1$ can be increased up to $\Delta B$ without significant linebroadening. In this case, we have

$$N_{\text{min, hom}} \cong \alpha \frac{T^{3/2} \sqrt{R}}{B_u B_0^3}$$

(1.6)
On the other hand, for inhomogeneously broadened lines, the spin sensitivity $N_{\text{min,inhom}}$ is approximately $N_{\text{min,hom}}$ from Equation 1.6 multiplied by the linewidth in Gauss. This is why the spin sensitivity is often expressed in $[\text{spins G}^{-1} \text{Hz}^{-1/2}]$. From Equation 1.6, it is evident that to increase the spin sensitivity, $B_u$ has to be optimized. In other words, for a given power, the magnetic field intensity $B_1$ has to be maximized. Another task will be to tune and match the different resonators used in this study.

1.3. Model

In this section, we develop an integral equation capable of solving the surface currents generated on the metallization patch of any CPW-structure for a given excitation. We are then able to compute the magnetic field from the surface current distribution obtained on the metallic structure. As will be seen later, this more advanced method compared to standard FDTD solvers available today is thought to be much faster for our present needs, i.e. for tuning and matching CPW-resonators. This is due to the rotational and translational symmetries of Green’s functions in stratified media, which allow a lot of precomputation, thus speeding up considerably the computation when just a small part of the structure is being modified (e.g. a capacitive gap thickness).

1.3.1. Model Assumptions

We assume a dielectric layer with dielectric constant $\epsilon_r = \epsilon'_r(1 - j\tan\delta)$ sandwiched between two open layer with $\epsilon_r = 1$. The dielectric layer is assumed infinite in the transverse direction. The substrate dielectric constant is here $\epsilon'_r = 3.38$ which corresponds to Rogers4003[11]. We neglect the metallization layer thickness. The loss tangent is taken as $\tan\delta = 2.7 \times 10^{-3}$. The dielectric substrate height is $h = 1.524 \text{mm}$. The vacuum frequency is maintained fixed at $f_0 = 10 \text{GHz}$ (X-band). It is in principle straightforward to sweep the frequency, but as will be seen in the following, we can precompute all the Green’s functions once at the beginning and retrieve them using an interpolation scheme as a function of the distance $\rho$. Moreover we assume that the sample is so small as not to influence the field distributions. We define the $z$ axis perpendicular to the plane of stratification (see Figure 1.1) and while $x$ and $y$ coordinates being in the transverse plane and equivalent by cylindrical symmetry. We place the origin of the coordinate system on the top of the dielectric layer. The medium permeability $\mu$ and permittivity $\epsilon$ are defined in
Equation 1.7 and Equation 1.8 respectively.

\[ \mu = \mu_0 \quad \forall z \]  

(1.7)

and

\[ \epsilon = \begin{cases} 
\epsilon_0 & \text{for } z < -h \\
\epsilon_r \epsilon_0 & \text{for } -h \leq z \leq 0 \\
\epsilon_0 & \text{for } z > 0 
\end{cases} \]  

(1.8)

1.3.2. Maxwell Equations

From now on we assume an harmonic time dependance and we write the fields as complex quantities in phasor notation. The actual time quantities \( C(t) \) are linked to the phasor quantities \( C \):

\[ C(t) = \sqrt{2} \text{Re}[Ce^{j\omega t}] \]  

(1.9)

In Chapter 1, all the fields are assumed classical, meaning that Maxwell’s equations (Equation 1.10 to Equation 1.13) apply.

\[ \nabla \times \mathbf{E} = -j\omega \mu \mathbf{H} \]  

(1.10)

\[ \nabla \times \mathbf{H} = j\omega \epsilon \mathbf{E} \]  

(1.11)

\[ \nabla \cdot \mathbf{E} = 0 \]  

(1.12)

\[ \nabla \cdot \mathbf{H} = 0 \]  

(1.13)

There are no inhomogeneous source terms in these equations. The sources are present only on the surfaces (they are volumeless) and their effect appears in the boundary conditions given by Equation 1.14 and Equation 1.15.

\[ \hat{z} \times (\mathbf{E}_3 - \mathbf{E}_2) = 0 \]  

(1.14)

\[ \hat{z} \times (\mathbf{H}_3 - \mathbf{H}_2) = \mathbf{J}_s \]  

(1.15)

The surface current \( \mathbf{J}_s \), which vanishes outside the surface \( S_0 \) of the upper conductor, is related to the surface charge density \( q_s \) by the two-dimensional continuity equation:

\[ \nabla_t \cdot \mathbf{J}_s + j\omega q_s = 0 \]  

(1.16)
Figure 1.1: Model used in the simulations. The medium permeability $\mu$ and permittivity $\epsilon$ are defined in Equation 1.7 and Equation 1.8 respectively. A dielectric substrate with complex relative dielectric permittivity $\epsilon_r$ is sandwiched between two half-space each having $\epsilon_r = 1$. The dielectric loss is taken into account by the parameter $\tan \delta$. For a lossless substrate, we would have $\tan \delta = 0$. Due to the stratified medium, we have here a cylindrical symmetry around the $z$-axis. A $x$-directed Hertzian dipole is depicted at the origin of the coordinate system ($z=0$) which is placed at the upper interface dielectric-air.
1.3.3. Potentials

The solutions of Maxwell’s equations are elegantly solved by the classical theory of potentials\[12\]. The magnetic field $H$ being solenoidal, a vector potential $A$ can be defined such that

$$ H = \frac{1}{\mu} \nabla \times A \quad (1.17) $$

Inserting now Equation 1.17 in Equation 1.10 leads to

$$ \nabla \times (E + j\omega A) = 0 \quad (1.18) $$

The expression in parentheses is now irrotational and can be used to define a scalar potential $V$:

$$ E = -j\omega A - \nabla V \quad (1.19) $$

Introducing now Equation 1.19 and Equation 1.17 into Equation 1.10 and Equation 1.11, we obtain that the potentials are themselves solutions of two homogeneous Helmholtz equations:

$$ (\nabla^2 + k^2) A = 0 \quad (1.20) $$

$$ (\nabla^2 + k^2) V = 0 \quad (1.21) $$

with $k^2 = \omega^2 \mu \varepsilon$ the squared wavenumber of the medium considered (free-space or dielectric substrate). Due to the cylindrical symmetry of the problem, we can write $k^2 = k^2_r + k^2_z$, where $k_r$ represents the radial part of the wavenumber $k$ whereas $k_z$ its vertical part \[13\].

1.3.4. Mixed Potential Integral Equation

The starting point of the Electric field integral equation (EFIE)\[2\] is the boundary condition enforced on the tangential electric field at the upper air-dielectric interface\[5\]:

$$ \hat{z} \times (E^a(r) + E^e(r)) = \hat{z} \times Z_s J_s(r) \quad (1.22) $$

---

\[1\] we use here the property that the divergence of the curl of any vector field $K$ is always zero, i.e. $\nabla \cdot (\nabla \times K) = 0 \quad \forall K$ and Equation 1.13

\[2\] Even if we are mainly interested in the magnetic field intensity, the Magnetic Field Integral Equation (MFIE) formulation won’t be used in this work. Indeed, this latter has proven numerically unstable for very thin conductor\[5\]. In this work, the magnetic field intensity will be derived from the surface currents computed with the EFIE and the appropriate Green’s function.
where \( \hat{z} \) is a unit vector normal to the dielectric plane, the total electric field being the sum of the excitation field \( \mathbf{E}^e \) and the scattered field \( \mathbf{E}^s \) generated by the surface current \( \mathbf{J}_s \) present on the metallization layer. A surface impedance \( Z_s \), taking the finite conductivity of the metal into account, is defined as \[13\]:

\[
Z_s = \frac{1 + j}{\sigma \delta}
\]  
(1.23)

where \( \delta = \sqrt{\frac{2}{\sigma \omega}} \) is the skindepth \[2\] and \( \sigma \) the metal conductivity. For an ideal conductor, the surface impedance \( Z_s \) is zero. For copper at 10 GHz we have \( \delta = 0.66 \mu \text{m} \) and \( \sigma = 5.813 \times 10^7 \text{ S/m} \), giving a surface impedance \( Z_s = (0.02606 + 0.02606j) \Omega \).

We reformulate now [Equation 1.22] using the vector and scalar potentials for the scattered electric field (see [Equation 1.19]):

\[
\mathbf{E}^e (\mathbf{r}) = -j \omega \mathbf{A} (\mathbf{r}) - \nabla V (\mathbf{r}) + Z_s \mathbf{J}_s (\mathbf{r})
\]  
(1.24)

We then express the potentials as surface integrals of Green’s functions \( G_A \) and \( G_V \):

\[
\mathbf{A} (\mathbf{r}) = \iint_S G_A (\mathbf{r} | \mathbf{r}') \cdot \mathbf{J}_s (\mathbf{r}') dS'
\]  
(1.25)

\[
V (\mathbf{r}) = \iint_S G_V (\mathbf{r} | \mathbf{r}') q_s (\mathbf{r}') dS'
\]  
(1.26)

where \( \mathbf{r} \) is the observation point and \( \mathbf{r}' \) the source point and the surface charge density \( q_s \) is expressed as a function of the surface current \( \mathbf{J}_s \) using [Equation 1.16]:

\[
q_s = \frac{1}{j \omega} \nabla t \cdot \mathbf{J}_s
\]  
(1.27)

The dyadic (or rank-two) Green’s function \( \mathbf{G}_A \) is the solution of the inhomogenous Helmholtz equation \[14\]:

\[
(\nabla^2 + k^2) \mathbf{G}_A (\mathbf{r} | \mathbf{r}') = -\mu \delta (\mathbf{r} - \mathbf{r} ')
\]  
(1.28)

with the unit dyadic \( \mathbf{I} = \hat{x} \hat{x} + \hat{y} \hat{y} + \hat{z} \hat{z} \).

Dyadics are second-rank tensors used to represent Green’s functions relating an arbitrary oriented elementary source (Hertz dipole) to the fields and vector potentials that it creates \[4\]. For instance, we get for the vector potential \( \mathbf{A} (\mathbf{r}) \):

\[
d\mathbf{A} (\mathbf{r}) = \mathbf{G}_A (\mathbf{r} | \mathbf{r}') \cdot I (\mathbf{r}') d'Y
\]  
(1.29)
The scalar component $G_{\text{st}}(r|r')$ gives the s components of the vector potential $A(r)$ created at the point $r$ by an elementary $t$-directed Hertzian dipole of unit moment $Idl' = 1$ and located at the point $r'$.

Due to the linearity of Maxwell’s equation, the superposition principle applies. This means that once the dyadic Green’s function $G_{\text{A}}$ or the scalar Green’s function $G_{\text{V}}$ are known, the general solutions $A(r)$ and $V(r)$ of an arbitrary surface current distribution are simply given by the surface integrals given by Equation 1.25 and Equation 1.26.

Finally, using Equation 1.27, Equation 1.25 and Equation 1.26, Equation 1.24 can be cast into:

$$\hat{z} \times E_e(r) = Z_s J_s(r) + \hat{z} \times \left( j\omega \int_{S'} G_{\text{A}}(r|r') \cdot J_s(r') dS' - \frac{1}{j\omega} \nabla \int_{S'} G_{\text{V}}(r|r') \nabla \cdot J_s(r') dS' \right)$$

(1.30)

which will be referred to as the Mixed Potential Integral Equation in the following.

### 1.3.5. Spectral Domain

The most efficient way to compute electromagnetic fields (and potentials) in a stratified medium is to transform the problem in the spectral domain, thus taking full advantage of the cylindrical symmetry of the medium[5, 15]. In the spectral domain, the transverse cartesian coordinates $x$ and $y$ of a function $f(x,y)$ are transformed to their spectral counterparts $k_x$ and $k_y$ while leaving the $z$ coordinate unaffected. The function $f(x,y)$ is related to its spectral counterpart $\tilde{f}(k_x,k_y)$ by the double Fourier transform:

$$\tilde{f}(k_x,k_y) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(x,y) e^{-jk_xx-jk_yy} dx dy$$

(1.31)

For the inverse transformation we have:

$$f(x,y) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \tilde{f}(k_x,k_y) e^{jk_xx+jk_yy} dk_x dk_y$$

(1.32)

With the change of variable

$$k_x = k_\rho \cos k_\phi \quad x = \rho \cos \phi$$
$$k_y = k_\rho \sin k_\phi \quad y = \rho \sin \phi$$

(1.33)

the exponential can be transformed to:

$$e^{jk_xx+jk_yy} = e^{j(k_\rho \rho \cos k_\phi \cos \phi + k_\rho \rho \sin k_\phi \sin \phi)} = e^{j(k_\rho \rho \cos(k_\phi - \phi)}$$

(1.34)
The inverse transformation in polar coordinates now reads:

$$f(\rho, \phi) = \frac{1}{2\pi} \int_0^{2\pi} \int_0^\infty dk_\rho k_\rho \tilde{f}(k_\rho, k_\phi) e^{jk_\rho \rho \cos(k_\phi - \phi)}$$

(1.35)

By rotational symmetry we have $\tilde{f}(k_\rho, k_\phi) = \tilde{f}(k_\rho)$. Using the Jacobi-Anger expansion:

$$e^{jk_\rho \rho \cos(k_\phi - \phi)} = \sum_{m=-\infty}^{\infty} (j)^m J_m(k_\rho \rho) e^{jm(k_\phi - \phi)}$$

(1.36)

where $J_m$ is the Bessel function of the first kind and the fact that

$$\int_0^{2\pi} d\phi e^{jm(k_\phi - \phi)} = \begin{cases} 0 & \text{if } m \neq 0 \\ 2\pi & \text{if } m = 0 \end{cases}$$

(1.37)

we end up with

$$f(r) = \int_0^\infty \tilde{f}(k_\rho) J_0(k_\rho \rho) k_\rho dk_\rho$$

(1.38)

which is the Sommerfeld Integral of order zero. This result can be generalised to higher order $n$ as defined in [Equation 1.44](#).

Due to the cylindrical symmetry, we can now introduce polar coordinates in the transverse plane and define the polar vector $\rho = x\hat{x} + y\hat{y}$. By the same token, we introduce the radial spectral variable $k_\rho = k_x\hat{x} + k_y\hat{y}$ which permits one to split the nabla operator

$$\nabla = \hat{x} \frac{d}{dx} + \hat{y} \frac{d}{dy} + \hat{z} \frac{d}{dz} = \nabla_t + \hat{z} \frac{d}{dz}$$

(1.39)

into

$$\tilde{\nabla} = jk_\rho + \hat{z} \frac{d}{dz}$$

(1.40)

The relevance of the spectral domain approach is clearly given by the fact that if a quantity $\Psi$ is solution of the homogeneous Helmholtz equation

$$(\nabla^2 + k^2) \Psi = 0$$

(1.41)

then its spectral transform $\tilde{\Psi}$ is a solution of the ordinary differential equation

$$\left(\frac{d^2}{dz^2} + k_z^2\right) \tilde{\Psi} = 0$$

(1.42)

with $k_z^2$ given by

$$k_z^2 = k^2 - (k_x^2 + k_y^2) = k^2 - k_\rho^2$$

(1.43)
1.3.6. Green’s Functions

In this subsection we give the expressions for the different Green’s functions needed to solve Equation 1.30. All Green’s functions are derived in the spectral domain, where the Helmholtz equations take a simpler form. The Sommerfeld Integral of order \(n\) is defined as:

\[
S_n[f] = \int_C \tilde{f}(k\rho)J_n(k\rho\rho)k_{\rho}^{n+1}dk_{\rho}
\]  \hspace{1cm} (1.44)

where \(C\) is a path in the complex plane of \(k\) from 0 to \(\infty\).

In this work, the only quantity we are interested in is the normal magnetic field \(H_z\) which is directly related to the unitary field \(B_u\) from Section 1.2. This latter is the quantity to be optimized for a given input power. The normal magnetic field generated by an \(x\)-directed elementary Hertzian dipole is Green’s function \(G_{zx}^{\perp}\) which, in the spectral domain, reads:

\[
\tilde{G}_{zx}^{\perp} = \frac{1}{4\pi}(1 + R_{TE})jk_y e^{-jkzz}
\]  \hspace{1cm} (1.45)

In the real space domain, we have

\[
G_{\perp x}^{\perp} = \frac{1}{4\pi} \sin \phi \ S_1 \left[ \frac{(1 + R_{TE})}{-jk_z} e^{-jkzz} \right]
\]  \hspace{1cm} (1.46)

with \(S_1\) the Sommerfeld Integral of order 1 as defined in Equation 1.44. In the following, we will fix the observer at \(z=100\ \mu m\) above the substrate.

The other field components can be derived in a similar way (for microstrip configuration, they are given extensively by Mosig and Sarkar in [13]). In this work, we assume a surface current present in the transverse direction only (\(x\)- or \(y\)-direction) meaning we don’t need Green’s functions for \(z\)-directed elementary Hertzian dipole. The scalar and vector potentials are rederived in Appendix A for coplanar configuration (CPW). At the upper interface \((z=0)\) we obtain for the components of the vector and scalar potentials:

\[
\tilde{G}_{A}^{\perp x} = \frac{1}{4\pi} \left(1 + R_{TE}\right) jk_z
\]  \hspace{1cm} (1.47)

\[
\tilde{G}_V = \frac{1}{4\pi \epsilon_0} \frac{1}{jk_z} \left( \frac{k_0^2 R_{TE} + k_z^2 R_{TM}}{k_{\rho}^2} + 1 \right)
\]  \hspace{1cm} (1.48)

which can be transformed back into the real space domain as:
\[
G_{xx}^{AA} = \frac{1}{4\pi} S_0 \left[ \frac{(1 + R_{TE})}{jk_z} \right] \\
G_V = \frac{1}{4\pi\epsilon_0} S_0 \left[ \frac{1}{jk_z} \left( \frac{k_{3}^2 R_{TE} + k_{3}^2 R_{TM}}{k_\rho^2} + 1 \right) \right]
\]
with \(S_0\) the Sommerfeld integral of order 0 as defined in [Equation 1.44]. By symmetry, we also have that \(G_{xx}^{AA} = G_{yy}^{AA}\). The Transverse Electric Fresnel Reflection Coefficient is given by [15]:

\[
R_{TE} = \frac{R_{12}^{TE} + R_{23}^{TE} e^{-2jk_zh}}{1 + R_{12}^{TE} R_{23}^{TE} e^{-2jk_zh}}
\]
with

\[
R_{12}^{TE} = \frac{\mu_2 k_{z1} - \mu_1 k_{z2}}{\mu_2 k_{z1} + \mu_1 k_{z2}}
\]

and

\[
R_{23}^{TE} = \frac{\mu_3 k_{z2} - \mu_2 k_{z3}}{\mu_3 k_{z2} + \mu_2 k_{z3}}
\]
here we have \(k_{z3} = k_{z1}\) and \(\mu_1 = \mu_2 = \mu_3 = 1\). In a similar way, we obtain for the Transverse Magnetic Fresnel Coefficients:

\[
R_{TM} = \frac{R_{12}^{TM} + R_{23}^{TM} e^{-2jk_zh}}{1 + R_{12}^{TM} R_{23}^{TM} e^{-2jk_zh}}
\]
with

\[
R_{12}^{TM} = \frac{\epsilon_{r2} k_{z1} - \epsilon_{r1} k_{z2}}{\epsilon_{r2} k_{z1} + \epsilon_{r1} k_{z2}}
\]

and

\[
R_{23}^{TM} = \frac{\epsilon_{r3} k_{z2} - \epsilon_{r2} k_{z3}}{\epsilon_{r3} k_{z2} + \epsilon_{r2} k_{z3}}
\]
here we have \(k_{z3} = k_{z1}\) and \(\epsilon_{r1} = \epsilon_{r3} = 1\) and \(\epsilon_{r2} = \epsilon_r\) as depicted on Figure 1.1.

Note that for microstrip configuration we would have \(R_{12}^{TE} = -1\) and \(R_{12}^{TM} = 1\) to describe the ground plane below the substrate (electric wall). When the source is not placed at the origin, Green’s function \(G_{H}^{xx}\) [Equation 1.46] is still valid provided the coordinates \(\rho\) be replaced by \(|\rho - \rho'|\) and \(\phi\) by the angle \(\zeta = \sin[\xi \sin(\phi - \phi')\sin(\phi')]/\xi\) (see Figure 1.2).

**Integration of Sommerfeld’s Integrals**

Contrary to Sommerfeld’s integrals appearing in the homogeneous case where an analytical solution exists, no such solution exists for stratified media and one has to recur to numerical integration[5]. The integration of Sommerfeld integrals are difficult to evaluate for two reasons:
1.3 Model

Figure 1.2.: Geometrical relationship to compute the angular dependence of $G^z_{\psi \phi} \zeta$ when the observation point $\rho$ and the source vector $\rho'$ are arbitrary. The source, here depicted by the white arrow, is a Hertzian dipole. When the source is not placed at the origin, Green’s function $G^z_{\psi \phi}$ (Equation 1.46) is still valid provided the coordinates $\rho$ be replaced by $|\rho - \rho'|$ and $\phi$ by the angle $\zeta = \sin\left[\frac{\rho \sin \phi - \rho' \sin \phi'}{\zeta}\right]$. Adapted from [16].

1. The spectral kernel can present poles.

2. They have an oscillatory tail (when $k_\rho \to \infty$)

The strategy chosen here is a deformation of the path integral in the first quadrant of the complex plane $0 \to P \to k_0 \sqrt{\epsilon_r}$ to avoid the poles of the denominator of the integrands. The poles are located on the real axis in the interval $[k_0, k_0 \sqrt{\epsilon_r}]$ [16] for lossless substrates but in the fourth quadrant of the complex $k_\rho$ plane for lossy substrates [5]. Physically, those poles represents surface waves which are bound to the interface dielectric-air, and can exist even in the absence of conductors [5][16]. Those surface waves particularly complicates the behaviour of the fields near the surface, where one should be cautious when using quasi-static near-field approximation [16]. The static parts of Green’s functions in the spectral domain are the asymptotic terms for $k_\rho \to \infty$. The extracted static parts can be transformed back into the space domain analytically by using Sommerfeld identity [17]:

$$
\int_C J_0 (k_\rho \rho) \frac{e^{-jk_z |z|}}{jk_z} k_\rho dk_\rho = \frac{e^{-jkr}}{r} \tag{1.57}
$$
and

\[ \int_C J_1 (k \rho) e^{-j k z} |z| d\rho = \frac{e^{-j kr}}{\rho} - \frac{|z|}{\rho e^{-j kr}} \]  

which can be derived by integration by parts.

### 1.3.7. Method of Moment

A standard way to solve Equation 1.30 is the Method of Moment (MoM) as introduced by Harrington [6]. The surface current is first expanded as a series of known basis functions, usually entire domain basis functions (for simple shape such as rectangular patches) or subsectional basis functions (for non-trivial metallization shapes). The surface charge density is then derived using the transverse continuity equation Equation 1.16. Then, the basic idea of the moment method consists in replacing boundary condition Equation 1.22 which, ideally, should be enforced everywhere on the metallization surface, by a set of approximate ones, obtained by "testing" Equation 1.22 with a set of weight (also called 'test') functions. If we choose to expand the surface current with \( N = N_x + N_y \) basis functions, and that we select \( N \) 'testing' functions, we can cast Equation 1.22 in a matrix form, where each row represents an enforced boundary condition on the surface of the metal and each column is related to a given surface current basis function. The matrix can be written as a generalize impedance linear system:
\[ Z \cdot I = V^e \quad (1.59) \]

or with the spatial dimensions \( x \) and \( y \) written explicitly:

\[
\begin{pmatrix}
Z_{xx} & Z_{xy} \\
Z_{yx} & Z_{yy}
\end{pmatrix}
\begin{pmatrix}
I_x \\
I_y
\end{pmatrix}
=
\begin{pmatrix}
V_x^e \\
V_y^e
\end{pmatrix}
(1.60)
\]

where the vector \( V^e \) is called the 'excitation' vector, \( Z \) the generalised impedance tensor and \( I \) is the vector containing the unknown coefficients of the surface current basis expansion.

To summarize, we need three sets of basis functions: one set for the surface current expansion, one for the surface charge density expansion (obtained from the latter by using the continuity equation [Equation 1.16]) and a set for 'testing' the boundary condition given by Equation 1.22.

In this work, we use a subsectional basis kernel with asymmetric rooftop functions \( T_i \) for the surface current expansion, and asymmetric 2D-pulse doublets \( \Pi_i \) for the surface charge density expansion. The 'testing' is done along a segment joining the centers \( r_i^- \) and \( r_i^+ \) of the current cells. This kind of 'testing' is usually called *razor-edge testing* [18, 19, 20].

The only unknown is the surface current \( J_s \) which is expanded with a subsectional basis. If the expansion contains \( N \) basis functions, we get:

\[ J_s = \sum_{i=1}^{N} \alpha_i T_i \quad (1.61) \]

The kernel of the basis are the rooftops function \( T_i \) which are defined as:

\[
T_i = \begin{cases} 
\hat{x} T_{ix}, & i = 1, \ldots, N_x \\
\hat{y} T_{iy}, & i = N_x + 1, \ldots, N
\end{cases}
(1.62)
\]

with

\[
T_{iu} = \begin{cases} 
1 - \frac{|u|}{d_{ui}} & \text{for } \rho \in S_{ui}^- \\
1 - \frac{|u|}{d_{uj}} & \text{for } \rho \in S_{uj}^+ \\
0 & \text{otherwise}
\end{cases}
(1.63)
\]
By using the two-dimensional continuity equation \([\text{Equation 1.16}]\) on \([\text{Equation 1.61}]\) we obtain for the basis function of the charge density \(q_s\) the pulse doublets \(\Pi_i = -\frac{1}{j\omega} \nabla \cdot T_i\) and for \(q_s\):

\[
q_s = \sum_{i=1}^{N} \alpha_i \Pi_i
\]

(1.64)

where the pulse doublets \(\Pi_i\) are defined as:

\[
\Pi_i = \begin{cases} 
\Pi_{ix}, & i = 1, \ldots, N_x \\
\Pi_{iy}, & i = N_x + 1, \ldots, N
\end{cases}
\]

(1.65)

with

\[
\Pi_{iu} = \begin{cases} 
\frac{j\omega}{d_{u1}} & \text{for } \rho \in S^{-}_{ui} \\
\frac{j\omega}{d_{u2}} & \text{for } \rho \in S^{+}_{uj} \\
0 & \text{otherwise}
\end{cases}
\]

(1.66)

Note that the surface current \(J_s\) is a vector quantity whereas the surface charge density \(q_s\) is a scalar.

Using rooftop functions for the current expansion and testing along segment \(C_i\) (razor-edge functions) defined in \(\text{Figure 1.5}\) the element \(Z_{ij} = a_{ij} + v_{ij} + l_{ij}\) of the generalized MoM-matrix \(Z\) in \(\text{Equation 1.60}\) are [5]

\[
a_{ij} = j\omega \int_{C_i} dl \int_{S_j} G_A(\rho|\rho') \cdot T_j(\rho') dS'
\]

(1.67)

\[
v_{ij} = \frac{1}{j\omega} \int_{S_j} \left[ G_v(\rho_i^+|\rho') - G_v(\rho_i^-|\rho') \right] \Pi_j(\rho') dS'
\]

(1.68)

\[
l_{ij} = Z_s \int_{C_i} T_j(\rho) \cdot dl
\]

(1.69)

where the last term takes Ohmic losses into account. In this work, the surface integrals were evaluated using two-dimensional Gaussian quadratures[21]. For the components of the excitation vector \(V_e^i\), we get

\[
V_e^i = \int_{C_i} E_e(\rho) \cdot dl
\]

(1.70)

The excitation mechanism used in this work is a voltage gap generator attached at the beginning of the CPW transmission line. It means the element of the excitation voltage vector \(V_e\) corresponding to the testing segment of the excitation is set to 1 V, while all other components are set to zero.
\[ \rho_{ui} - \rho_{ui} = \rho_{ui} + \rho_{ui} - \rho_{ui} + \rho_{ui} - C_i = i \]

Figure 1.4: Definition of the current cells used in the discretization of the metallization sheet. A u-directed current cell \( S_{ui} \) is defined by the union of two elementary charge cells \( S_{ui}^- \) and \( S_{ui}^+ \). Besides, a current cell is characterized by its position \( \rho_{ui} \) and its longitudinal dimensions \( du_{i1} \) and \( du_{i2} \) and its transverse dimension \( dv_i \). For x-directed current cells, \( (u,v) \equiv (x,y) \) whereas for y-directed current cells, \( (u,v) \equiv (y,x) \). The testing segment \( C_i \) is also depicted by the dashed line.
Figure 1.5: Definition of the three different basis functions used to solve Equation 1.30: a) rooftop basis function $T_i$ (defined in Equation 1.62) used in the expansion of the surface current $J_s$; b) 2D-pulse doublets $\Pi_i$ (defined in Equation 1.65) used in the expansion of the charge density $q_s$; c) razor-edge test functions $C_i$ used to test along the segment joining $\rho_{iu}^- \rightarrow \rho_{iu}^+$ (see Figure 1.4).
1.3.8. Implementation

Structure Dimensions

The total length (y-direction) $L_S$ of the metallization is 3 cm whereas its total width $W_S$ is 1.02 cm. The sum length of the CPW-line and the resonator was fixed to 1.2 cm. In all simulations, the resonators were fed by a CPW-line with characteristic dimensions $W_L = 1.4$ mm and a gap between the ground and center conductor of $G_{L1} = 100$ µm. Those dimensions correspond to a characteristic line impedance of 50 Ω at 10 GHz. The matching of the resonator to the line is done via the matching gap $G_{L2}$.

Meshing

The metallization patch was discretized into elementary rectangular cells (staircase approximation). The number of elementary cells used was such as to fulfill the criterion of a minimum of ten cells per free space wavelength.[22] The $1/r$ singularity extracted from the static part of Green’s functions (Equation 1.57) was integrated analytically as a function of the cells dimensions and the source-observer distance $\rho$.[18]

Transmission Line Reflection Parameter $S_{11}$

The input impedance $Z_{in}$ at the beginning of the transmission line is obtained as the ratio of the excitation voltage and the current flowing in the excitation cell $i = I$, which equals the expansion coefficient $\alpha_I$ (see Equation 1.61):

$$Z_{in} = \frac{V}{\alpha_I} \quad (1.71)$$

The reflection parameter $S_{11}$ is computed from the input impedance as ([2]):

$$S_{11} = \frac{Z_{in} - 50}{Z_{in} + 50} \quad (1.72)$$

Speeding up Computations

First, because Green’s functions only depend on the substrate height $h$ and on its dielectric constant $\epsilon_r$ which are kept constant here, we can precompute and store them as a function of the source-observer distance $\rho$.[31]. Green’s functions appearing in the surface integrals of the
Figure 1.6: Characteristic dimensions for the opened-\(\lambda/2\) resonators. The ground metallization sheet length \(L_G=3\, \text{cm}\) whereas its width \(W_G=1.02\, \text{cm}\). The CPW-waveguide is characterized by the center conductor thickness \(W_L=1.4\, \text{mm}\) and the gap between the center strip and the ground \(G_{L1}=0.1\, \text{mm}\) which giving for the transmission line a characteristic impedance of about 50 Ohm at 10 GHz. The resonator itself is matched to the transmission line with the two capacitive gaps \(G_{L2}\). It is characterized by its length \(R_L\), the constant lengths \(L_{R1}=1\, \text{mm}\) and the parameters under study in this work: the inner loop diameter \(D_{Ri}\), the outer loop diameter \(D_{Ro}\) chosen such that the loop thickness equals 100\(\mu\text{m}\) and the loop gap \(G_R\).
Figure 1.7: Characteristic dimensions for the shorted-\(\lambda/4\) resonators. The dimensions are as in Figure 1.6 except \(L_{R1} = 433\,\mu m\). Instead of being open at the top-end of the transmission line, the resonator is now shorted, meaning only one matching gap \(G_{L2}\) is present. Its length \(L_R\) is also about twice as short as the one for the opened-\(\lambda/2\) one.
MPIE (Equation 1.30), can then be retrieved by an interpolation scheme (in this work we use cubic-spline). To avoid to recompute Green’s functions every time, and because we are only interested in the working frequency \( f_0 = 10 \text{ GHz} \), we also keep \( f_0 \) constant (as recommended in \[5\]). In our case, this means that instead of sweeping the frequency \( f \) to look for resonances, we change the resonator length until we observe a strong minimum in the reflection coefficient \( S_{11} \) (Equation 1.72).

Second, the whole content of the matrix, which contains many redundant elements, can be stored in a compact form using a special mapping scheme. This mapping is based on the parity (even or odd) of the current- (roof-top), charge- (2D-pulse doublets), and test- (razor-edge) basis functions. If we place the origin of the coordinate system on the source cell, then depending on which quadrant the observation cells is located, a simple relationship for the four cases can be found where only a sign change is needed (see \[7\] for further details).

Third, when matching and tuning the structures, the whole MoM matrix needs to be computed once only at the beginning. For all subsequent runs, where the resonator lengths and matching gaps are screened, we need to recompute only the elements of the Moment Matrix corresponding to surface current cells at the edge of the resonators and around the gap respectively. When the dimensions of a current cell are modified, only the corresponding row and column need to be recomputed. Moreover, the use of the mapping law just described permits to reduce the number of elements to be recomputed to a strict minimum. This corresponds to a considerable time-improvement factor when optimizing a tiny part of the structure. This property has also been used in the context of electromagnetic optimization based on multistructures where one subsequently suppresses a current cell\[23\].

Finally, to solve the MoM linear system, we used the Automatically Tuned Linear Algebra Software (ATLAS)\[24\] library which is a machine-optimized version of the Basic Linear Algebra Subprograms (BLAS)\[25\] [26] as well as the Linear Algebra Package (LAPACK)\[27\].
Computation of the Magnetic Field

Once the coefficients of the surface current expansion are known, the normal component of the magnetic field can be computed at any given observation point \( r \) as follows:

\[
H_z(r) = \sum_{i=1}^{N_x=N_x+N_y} \int_{S_i} G_{zz}^H(r|r') \cdot J_s(r') dS' \quad (1.73)
\]

\[
= \sum_{i=1}^{N_x} \int_{S_{ix}} G_{zx}^H(r|r') J_{sx}(r') dS' + \sum_{i=1}^{N_y} \int_{S_{iy}} G_{zy}^H(r|r') J_{sy}(r') dS' \quad (1.74)
\]

As already explained in Subsection 1.3.6 we use the change of variable defined in Figure 1.2. Note that the distance is now \( r = \sqrt{\rho^2 + z^2} \) with \( z=100 \mu m \) above the substrate. Moreover, it is known that the Sommerfeld Integral required to compute \( G_{zz}^H \) back in the real space domain is not convergent for \( z=0 \) (see [5]). The integral must then be evaluated in the sense of distribution in the limit \( \lim_{z \to 0} \) where the exponential factor \( e^{-jk_z z} \) in Equation 1.46 ensures convergence. With our choice of \( z = 100 \mu m \) we need not worry about this problem.

1.4. Results

In this section we present the results of the numerical simulations for the normal magnetic fields along with the surface current distributions. All the resonators were tuned and matched by varying the resonator length and the capacitive gaps \( G_{L1} \) respectively. We first tuned the resonators by fixing the matching gap \( G_{L1} \) to a value of 100 \( \mu \)m and swept the resonator length to find a minimum in the reflection coefficient \( S_{11} \). This latter was obtained by first computing the input impedance \( Z_{in} \) from the computed surface current flowing in the excitation cell using Equation 1.71 and then by using Equation 1.72. At the resonator length corresponding to a minimum \( S_{11} \) we then changed the width of the two gaps \( G_{L1} \) (for the \( \lambda/2 \) open resonators) and the gap \( G_{L1} \) (for the \( \lambda/4 \)-shorted resonators) and looked for a minimum. The criterium for a good matching was a reflection coefficient \( S_{11} \) below -30 dB. During the tuning and matching process, only the elements of the Method of Moment matrix corresponding to the cells at the edge of the resonators and around the matching gaps needed to be recomputed. This strategy allowed a considerable gain in terms of computation time. Finally, using Equation 1.73, we computed the normal component of the magnetic field \( H_z \) intensity and phase from the computed surface current at a distance \( z=100 \mu m \) above the substrate. In the following, the real and imaginary
parts of the surface current distribution around the microcoil will also be depicted in blue and red respectively.

In Table 1.1 we list the different physical dimensions which were kept constant during the numerical computations. The center strip thickness $W_L$ and interstrip gaps $G_{L1}$ are chosen such as to have a 50 $\Omega$ line impedance at 10 GHz for a 1.524 mm thick Rogers4003 substrate ($\epsilon_r' = 3.38$ and $\tan\delta = 2.7 \times 10^{-3}$ at 10 GHz) and a copper metallization layer (conductivity $\sigma = 5.813 \times 10^7$ S/m at 10 GHz).

<table>
<thead>
<tr>
<th>$L_G$</th>
<th>3 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W_G$</td>
<td>1.02 cm</td>
</tr>
<tr>
<td>$L_L$</td>
<td>1.2 cm</td>
</tr>
<tr>
<td>$W_L$</td>
<td>1.4 mm</td>
</tr>
<tr>
<td>$G_{L1}$</td>
<td>0.1 mm</td>
</tr>
</tbody>
</table>

Table 1.1: Fixed parameters used in the numerical study for both $\lambda/2$ and $\lambda/4$ resonators (see also Figure 1.6 and Figure 1.7).

1.4.1. Open $\lambda/2$ resonator

Here we simulate CPW $\lambda/2$ microresonators which are terminated by two gaps, one matching the resonator to the transmission line, and one matching the resonator to the ground. When matching and tuning, we keep the thickness of those gaps equal to $G_{L1}$ for both gaps. We study the influence of the loop diameter $D_{Ri}$ and the loop gap $G_R$ (see Figure 1.6) on the magnetic field intensity for tuned and matched resonators. In Section 1.5 we compare the field obtained for the open-$\lambda/2$ loop diameter $D_{Ri}=100 \mu$m and a loop gap $G_R=100 \mu$m from Section 1.4.1 with the commercial FDTD software CST-Microwave Studio[28].
1.4 Results

Loop Diameter $D_{Ri} = 100 \mu m$, Loop Gap $G_R = 100 \mu m$

Figure 1.8 shows the normal field intensity $\text{Abs}(H_z)$ and its phase over the resonator computed at a distance $z = 100 \mu m$ above the substrate.

**Figure 1.8:** Magnetic field $H_z$ a) intensity and b) phase for a $\lambda/2$ open resonator with a loop diameter $D_{Ri}$ of 100 $\mu m$ and a gap thickness $G_R$ of 100 $\mu m$ computed on resonance and $z=100 \mu m$ above the dielectric substrate. The working frequency is set to $f_0 = 10 \text{ GHz}$. c) real and d) imaginary part of the surface current distribution around the loop.
Loop Diameter $D_{RI}=200 \mu m$, Loop Gap $G_R=100 \mu m$

Figure 1.9.: Magnetic field $H_z$ a) intensity and b) phase for a $\lambda/2$ open resonator with a loop diameter $D_{RI}$ of 200$\mu m$ and a gap thickness $G_R$ of 100$\mu m$ computed on resonance and $z=100\mu m$ above the dielectric substrate. The working frequency is set to $f_0 = 10$ GHz. c) real and d) imaginary part of the surface current distribution around the loop.
Loop Diameter $D_{Ri}=300 \mu m$, Loop Gap $G_R=100 \mu m$

**Figure 1.10.:** Magnetic field $H_z$ a)intensity and b)phase for a $\lambda/2$ open resonator with a loop diameter $D_{Ri}$ of 300\,$\mu$m and a gap thickness $G_R$ of 100\,$\mu$m computed on resonance and $z=100\,\mu$m above the dielectric substrate. The working frequency is set to $f_0 = 10$ GHz. c)real and d)imaginary part of the surface current distribution around the loop.
Loop Diameter $D_{Ri} = 200 \mu m$, Loop Gap $G_{R} = 200 \mu m$

Figure 1.11.: Magnetic field $H_z$ a) intensity and b) phase for a $\lambda/2$ open resonator with a loop diameter $D_{Ri}$ of 200 $\mu m$ and a gap thickness $G_R$ of 200 $\mu m$ computed on resonance and $z=100 \mu m$ above the dielectric substrate. The working frequency is set to $f_0 = 10 \text{ GHz}$. c) real and d) imaginary part of the surface current distribution around the loop.
1.4.2. Short-circuited λ/4 resonator

Loop Diameter $D_{Ri}=100 \, \mu m$, Loop Gap $G_R=100 \, \mu m$

**Figure 1.12.** Magnetic field $H_z$ a) intensity and b) phase for a $\lambda/4$ shorted resonator with a loop diameter $D_{Ri}$ of $100 \, \mu m$ and a gap thickness $G_R$ of $100 \, \mu m$ computed on resonance and $z=100 \, \mu m$ above the dielectric substrate. The working frequency is set to $f_0 = 10 \, \text{GHz}$. c) real and d) imaginary part of the surface current distribution around the loop.
Loop Diameter $D_R = 200\ \mu\text{m}$, Loop Gap $G_R = 100\ \mu\text{m}$

Figure 1.13.: Magnetic field $H_z$ a) intensity and b) phase for a $\lambda/4$ shorted resonator with a loop diameter $D_R$ of 200\,$\mu$m and a gap thickness $G_R$ of 100\,$\mu$m computed on resonance and $z=100\ \mu$m above the dielectric substrate. The working frequency is set to $f_0 = 10\ \text{GHz}$. c) real and d) imaginary part of the surface current distribution around the loop.
Loop Diameter $D_{RI}=300 \, \mu m$, Loop Gap $G_R=100 \, \mu m$

Figure 1.14.: Magnetic field $H_z$ a)intensity and b)phase for a $\lambda/4$ shorted resonator with a loop diameter $D_{RI}$ of $300 \, \mu m$ and a gap thickness $G_R$ of $100 \, \mu m$ computed on resonance and $z=100 \, \mu m$ above the dielectric substrate. The working frequency is set to $f_0 = 10 \, GHz$. c)real and d)imaginary part of the surface current distribution around the loop.
Loop Diameter \( D_R = 200 \, \mu m \), Loop Gap \( G_R = 200 \, \mu m \)

**Figure 1.15:** Magnetic field \( H_z \) a) intensity and b) phase for a \( \lambda/4 \) shorted resonator with a loop diameter \( D_R \) of 200 \( \mu m \) and a gap thickness \( G_R \) of 200 \( \mu m \) computed on resonance and \( z = 100 \, \mu m \) above the dielectric substrate. The working frequency is set to \( f_0 = 10 \, \text{GHz} \). c) real and d) imaginary part of the surface current distribution around the loop.
1.5 CST Microwave Studio Simulations

Here we simulate the same $\lambda/2$-open resonator as in Section 1.4.1 with CST Microwave Studio\textsuperscript{28}. We used an hexahedral mesh type and the parameters “Lines per wavelength”=19, “Lower mesh limit”=21 and “Mesh line ratio limit”=50 giving a total of 119’700 Meshcells. We used for the boundary conditions ”open(add space)” above and below the substrate and ”open” otherwise. A waveguide port was set for the excitation and placed at the beginning of the CPW-line. The frequency range was chosen from 6 to 12 GHz. We used the transient solver with an accuracy of -30dB. One simulation run time was about 2 hours. We optimized the matching gap in the range 50 to 300 $\mu$m for a total time of about 20 hours and found a matching gap of 200 $\mu$m which is quite less than the 370 $\mu$m found with the MPIE solver. This parameter is clearly the most sensitive part of the structure and can vary considerably if convergence has not been met.
Figure 1.17: Reflection parameter $S_{11}$ obtained with a matching gap of 200 $\mu$m. With a total resonator length of 6.636 mm we get a resonance frequency $f_0=9.9581$ GHz and at that frequency a reflection coefficient $S_{11}$ of -21 dB.

Figure 1.18: Magnetic field for a 200 $\mu$m loop diameter and a 200 $\mu$m gap thickness computed on resonance ($f_0=9.9581$ GHz) and $z=100$ $\mu$m above the dielectric substrate (compare with Figure 1.8). The input power is 1 W.
Figure 1.19: Surface current generated on resonance ($f_0 = 9.9581$ GHz) at the air-dielectric interface for the same parameters as in Figure 1.18.

Table 1.2: Summary of the different computed resonators. The excitation power was 2.5 mW. The working frequency has been fixed to $f_0 = 10$ GHz. The second columns shows the resonator length $L_r$, the third the matching gaps $G_{L2}$ and $S_{11,min}$ the minimum reflection coefficients found on resonance. For the geometrical parameters $D_{Ri}, D_{Ro}$ and $G_R$, please refer to Figure 1.6 and Figure 1.7. The last column gives the maximum magnetic field intensity.
1.6. Summary

We observe the largest magnetic field intensity for $D_{Ri}=200 \mu m$ instead of $D_{Ri}=100 \mu m$. This may be due to the fact that we use a loop gap $G_R=100 \mu m$ for both and that the loop for the $D_{Ri}=100 \mu m$ is just a half-loop. Another possible explanation could be that as the diameter of the loop gets larger, its distance to the ground plane gets smaller, meaning that we have a supplementary capacitance coming into play which could influence the field distribution. Note that this effect is not present when using microstrip configuration, with the ground plane below the dielectric substrate. A good point is the absence of any phase-dispersion present in the center of the loop, which is the location of the sample.

The magnetic field intensity of the $\lambda/4$ resonators show again the same behaviour as a function of the loop diameter and the loop gap. We again find a maximum field intensity for the $D_{Ri}=200 \mu m$ resonator. Overall, we note that the values for the maximum field intensity are all a bit lower than the one for the $\lambda/2$ resonators. This may be due to the asymmetry in the field distribution (as seen on all field intensity simulations). We note that the magnetic field phase for the $\lambda/4$ resonators exhibits a completely different behaviour compared to the one for the $\lambda/2$ resonators. Again, no phase-dispersion is observed in the center of the loop. The time factor gained when optimizing compared to Microwave studio was up to 50.

1.7. Conclusion

We have presented a powerful full-wave solver for CPW-microcoil resonators based on the mixed-potential integral equation (MPIE). This model contains Ohmic losses as well as dielectric and radiation losses. The information of the stratified medium is contained in the Green’s functions which are the kernels of the MPIE. They are evaluated only once at the beginning of each optimisation run. The Moment Matrix could also be mapped into a very efficient algorithm avoiding the evaluation of redundant terms. The time gained with this strategy is considerable compared to standard FDTD softwares which are extremely time-consuming for optimization purposes.

With the solver developed, we have studied different microcoil resonators based on coplanar technology (CPW). The spin sensitivity of such a sensor is directly proportional to the magnetic
field intensity generated in the loop for a fixed source power. To this end, we computed the normal component of the magnetic field intensity of eight different resonators, four $\lambda/2$- and four $\lambda/4$-resonators.

We found the $\lambda/4$-resonators maximum field intensity is a bit less compared to the $\lambda/2$-resonators for the same excitation. This may be due to a field inhomogeneity at the top-end of the $\lambda/4$-resonators as can be seen on the simulations.

1.8. Outlook

To sum up, this numerical study has shown that the magnetic field intensity generated inside the microcoil of both $\lambda/2$ and $\lambda/4$-resonators is of about the same order of magnitude, meaning that both types of resonators should lead to similar spin sensitivity.

With the model developed in this work, it is an easy matter to back the opposite side of the dielectric by a ground plane by setting $R_{12}^{\text{TE}} = -1$ and $R_{12}^{\text{TM}} = 1$ as explained in Subsection 1.3.6, meaning microstrip- or CPW-Grounded resonators could be studied as well. In this work, we used rectangular current cells for ease of implementation. When working with rounded shapes it may be advantageous to use triangular current cells (as in [17]).

Finally, those resonators are foreseen to have applications in the fields of electron spin resonance as well as nanoelectronics, spintronics, and quantum information processing.
2. Decoupling during TOBSY Sequences

2.1. Introduction

In solid-state NMR under magic-angle spinning, the use of rotor-synchronised symmetry-based sequences is now a well-established way to tailor a specific effective Hamiltonian\cite{29}. Those techniques have been derived under the assumption of perfect decoupling, though. The issue of decoupling abundant spins I (e.g. $^1$H), when a symmetry-based sequence is applied to spins S (e.g. $^{13}$C) is a critical one and strongly influences the viability of the sequence.

It has been shown\cite{30} that this heteronuclear decoupling can be achieved by the recoupling sequences (i.e. without decoupling) or by a strong irradiation on the I spins. In this contribution we are concerned with the second one. Until recently, only continuous-wave irradiation was used. Indeed, in order to minimize interference effects between both channels, the cycle time of the I spins sequence should be as short as possible. This calls naturally for strong continuous wave (CW) irradiation. Besides, it is known that a condition for good heteronuclear decoupling is an rf-field intensity on the protons at least three times higher than the one on the carbons channel\cite{31,32}.

We have recently demonstrated theoretically and experimentally that a symmetry-based XiX\cite{33} modulation on the I-spins channel could lead to enhanced polarization transfer during a specific isotropic mixing sequence (PC9$_6^{1}$\cite{34}).

In this section we first give a short survey of the theory behind the symmetry-based sequences. We then focuse more specifically on homonuclear isotropic J-transfer sequences also known as total through bond correlation spectroscopy (TOBSY)\cite{35}. In Section 2.6 we propose a way to improve the polarization transfer under continuous-wave decoupling by using a supercycled
version of the PC9 sequence (PSC9). In Section 2.7 we study thoroughly the possibility of decoupling the protons by using an XiX-scheme. We demonstrate experimentally and numerically that for specific XiX-modulation frequencies, $\nu_{m,\text{XiX}} = \nu_t$ and $\nu_{m,\text{XiX}} = \nu_1, S$, we observe an enhanced polarization transfer.

In Section 2.8 we express the interesting condition $\nu_{m,\text{XiX}} = \nu_1, S$ in the dual channels symmetry-based form PC9\textsuperscript{1}C\textsuperscript{N}\textsuperscript{6} where a C-element is the concatenation of two rectangular pulses of arbitrary flip-angle (denoted here "L"), the second-one being $\pi$-phase-shifted with respect to the first one, thus generalizing the results obtained for XiX-decoupling. We use then Levitt’s Mathematica package\textsuperscript{36} to find the symmetry numbers $N$ and $\nu$ giving purely isotropic sequences. Those sequences are subsequently numerically tested using the GAMMA\textsuperscript{37} environment.

### 2.2. Spin Hamiltonian

In this section we list the different interactions relevant to Chapter 2 and Chapter 3. The spin Hamiltonian reads:

$$
\mathcal{H} = \mathcal{H}_{CS} + \mathcal{H}_D + \mathcal{H}_J + \mathcal{H}_{rf}
$$

(2.1)

the first term being the chemical-shift Hamiltonian, the second the dipolar Hamiltonian, the third the scalar coupling (or J-coupling) Hamiltonian and the last the radiofrequency Hamiltonian. If not stated otherwise, all the Hamiltonians are expressed in angular frequency units. Besides, the quantities expressed in angular frequency units are denoted by $\omega$ while quantities in natural frequency units are denoted by $\omega/2\pi$ or $\nu$.

#### 2.2.1. Chemical-Shift Hamiltonian

$$
\mathcal{H}_{cs} = \sum_k I_k \cdot (-\gamma_k) \mathbf{g}^k \cdot \mathbf{B}
$$

(2.2)

with the chemical-shift tensor $\mathbf{g}^k$. By choosing the main field $\mathbf{B}$ along the $+z$ axis $\mathbf{B} = (0, 0, B_0)$ and with the Larmor frequency $\omega_{0k} = -\gamma_k B_0$, the laboratory-frame chemical-shift Hamiltonian is

$$
\mathcal{H}_{cs} = \sum_k \omega_{0k}(\sigma_{zz}^k I_{kx} + \sigma_{yz}^k I_{ky} + \sigma_{zz}^k I_{kz})
$$

(2.3)
with the high-field approximation, the transverse terms are non-secular and can be neglected:

\[ H_{CS} = \sum_k (\sigma_{2k}^l \omega_{0k} I_{kz}) \]  

(2.4)

### 2.2.2. J-Coupling Hamiltonian

In diamagnetic substances, all the electronic shells being closed, the total electron spin is zero\[38\]. Therefore, in first order, the nuclear spins are completely decoupled from the electrons spins. There is, however, in second order, an apparent coupling of nuclei among themselves, the so-called indirect (or J-, or scalar) coupling, mediated by the binding electrons. The J-coupling Hamiltonian between spins \( I_k \) and \( I_n \) reads:

\[ H^{(k,n)}_J = 2\pi I_k J^{k,n} I_n \]  

(2.5)

where \( J^{k,n} \) is a tensor which describes the interaction. Note that in solid this interaction may be anisotropic contrary to liquid-state NMR where the anisotropic part is averaged out by molecular tumbling, leaving only the isotropic part.

### 2.2.3. Dipolar-Coupling Hamiltonian

Classically, the interaction energy between two magnetic dipole moments \( \mu_k \) and \( \mu_n \) separated by the internuclear vector \( r_{kn} \) reads:

\[ E^{kn}_D = \frac{\mu_0}{4\pi} \frac{1}{r_{kn}^3} \left( \mu_k \cdot \mu_n - \frac{3}{r_{kn}^2} (\mu_k \cdot r_{kn})(\mu_n \cdot r_{kn}) \right) \]  

(2.6)

Using Bohr’s correspondence principle, i.e. replacing each moment \( \mu \) by its operator form \( \gamma_k I \), we find for the dipolar Hamiltonian\[1\]

\[ H^{kn}_D = -\frac{\mu_0}{4\pi} \frac{\gamma_k \gamma_n \hbar}{r_{kn}^3} \left( I_k \cdot I_n - \frac{3}{r_{kn}^2} (I_k \cdot r_{kn})(I_n \cdot r_{kn}) \right) \]  

(2.7)

which can also be written as

\[ H^{kn}_D = I_k D^{(k,n)} I_n \]  

(2.8)

where \( D^{(k,n)} \) is a traceless tensor.

---

\[ ^1 \text{We don’t use any specific notation for operators. This should be evident from the context.} \]
2.2 Spin Hamiltonian

From now on, we define the dipolar strength $d$ in [Hz] as

$$d \equiv \frac{\mu_0 \gamma_k \gamma_n \hbar}{4\pi r_{kn}^3} \quad (2.9)$$

Expanding Equation 2.7 as a dipolar alphabet and keeping only the secular terms we get in the homonuclear case:

$$H_{D}^{kn} = -\frac{\mu_0 \gamma_k \gamma_n \hbar}{4\pi r_{kn}^3} P_2 \left(\cos \theta_{kn}\right) \left(2I_{kz}I_{nz} - \frac{1}{2}(I_k^+I_n^- + I_k^-I_n^+)\right) \quad (2.10)$$

while in the heteronuclear case, where the non-secular flip-flop terms average out:

$$H_{D}^{kn} = -\frac{\mu_0 \gamma_k \gamma_n \hbar}{4\pi r_{kn}^3} P_2 \left(\cos \theta_{kn}\right) \left(2I_{kz}I_{nz}\right) \quad (2.11)$$

with $\theta_{kn}$ the angle between the internuclear vector $r_{kn}$ and the $B_0$ field direction (+z-axis) and $P_2(\cos \theta_{kn}) = \frac{1}{2}(3 \cos^2 \theta_{kn} - 1)$ the second-order Legendre polynomial.

2.2.4. Rf Hamiltonian

The radiofrequency field $B_1(t)$ applied perpendicularly to the main field $B_0$ to a spin species $I$ is characterized by its amplitude $\omega_1(t)$, its phase $\phi(t)$ and its offset $\Delta \omega(t)$ from a reference frequency $\omega_0$. The most general form of the rf Hamiltonian in the Zeeman frame is

$$H_{rf}^{I}(t) = \omega_1(t)(\cos \phi(t) F_x + \sin \phi(t) F_y) + \Delta \omega(t)F_z \quad (2.12)$$

with $F_\alpha$ with $\alpha = x, y$ or $z$, denoting the total spin operator (e.g. $F_x = \sum_i I_{x,i}$ for an ensemble of $N$ spins).

2.2.5. Frame Transformations

When using Euler transformations it is advantageous to express the different interactions as irreducible spherical tensors\[39\]. To obtain a scalar Hamiltonian from two tensors quantities, the spatial tensor $A$ and the spin tensor $T$, a scalar product can be defined if the tensor quantities are expressed as vectors\[40\]. The Hamiltonian is then the sum over all interactions $i$ as follows:

$$H = \sum_i \sum_{l=0}^2 A_{i}^{(i)} \cdot T_{l}^{(i)} = \sum_i \sum_{l=0}^2 \sum_{q=-l}^{l} (-1)^q A_{lq}^{(i)} T_{l,-q}^{(i)} \quad (2.13)$$

In the rotating frame, to a very good approximation, all the non-secular terms with $q \neq 0$ average out and we get the high-field Hamiltonian:
\[ \mathcal{H} = \sum_i \sum_{l=0}^2 A_{l0}^{(i)} T_{l0}^{(i)} \quad (2.14) \]

**Static Case**

The interactions take their simplest form in a so-called principal axis system (PAS). In this frame, the space part of the dipolar interaction or of the symmetric part of the chemical-shift anisotropy are diagonal. To transform the spatial components of any interaction from its principal axis system to the laboratory frame, we perform an Euler transformation \( (\alpha, \beta, \gamma) \):

\[ A_{lm}^{\text{LAB}} = \sum_{m'=\pm l} A_{l'm'}^{\text{PAS}} e^{-i\alpha m'} d_{m'm}^{(\beta)} e^{-i\gamma m} \quad (2.15) \]

with \( d \), the reduced Wigner elements\(^41\).

**Under Magic-Angle Spinning**

In the case of magic-angle spinning, we use an intermediary frame, called rotor axis system (RAS). This means we use two different Euler transformations applied successively: \( (\alpha, \beta, \gamma) \) to transform from the PAS to the RAS, followed by \( (-\omega_r t, -\theta_m, 0) \) to transform from the RAS to the LAB frame:

\[ A_{lm}^{\text{LAB}}(t) = \sum_{m'=\pm l} A_{l'm'}^{\text{RAS}} e^{i\omega_r m'} d_{m'm}^{(\theta_m)} \quad (2.17) \]

with \( \omega_r \) the angular spinning frequency and \( \theta_m \) the magic angle \( \theta_m = \arctan(\sqrt{2}) \approx 54.7^\circ \). Note that after the second transformation, a time dependence appears due to magic-angle spinning. This latter affects only rank 2 tensors, though, leaving isotropic (scalar) interaction unaffected.

**2.2.6. Liouville - von Neumann Equation**

The evolution of the density matrix is governed by the Liouville-von Neumann equation \(^42\):

\[ \frac{d}{dt} \sigma(t) = -i [\mathcal{H}(t), \sigma(t)] \quad (2.18) \]
This equation is integrated numerically in the GAMMA\textsuperscript{37} environnement, by assuming step-wise constant Hamiltonians.

### 2.3. C/R Theory

The symmetry-based sequences $CN^\nu_n$ and $RN^\nu_n$\textsuperscript{29} take advantage of interference effects between spin- and real-space in magic-angle spinning solid state nuclear magnetic resonance. By a judicious choice of the symmetry numbers $N$, $n$ and $\nu$ it can be shown using average Hamiltonian theory\textsuperscript{43}, that they can generate effective spin Hamiltonians containing only specific interactions\textsuperscript{44}. The idea is that a time interval spanning $n$ rotor periods is subdivided into $N$ C-elements. The phase of each C-element is then successively advanced by $2\pi \cdot \nu/N$. A C-element can be any pulse sequence element performing a multiple of $2\pi$ rotation of the nuclear spins around the $x$-axis, zero included. In a $CN^\nu_n$, the symmetry numbers $n$ and $\nu$ are called the space and spin winding numbers respectively. Figure 2.1 shows an example of a C-sequence, a $C7^1_2$ used in $\gamma$-encoded homonuclear double-quantum recoupling. The specific relationship between space- and spin-rotation is evident from the pictorial representation: one spin rotation (spin winding number $\nu=1$) is performed while the rotor performs two revolutions (space winding number $n=2$). Note that the spin-rotation is discrete, while the space one is continuous (mechanical rotation of the sample).

![Graphical representation of the sequence $C7^1_2$. The helix corresponding to the spatial rotation is continuous whereas the one for the spin rotation is discrete and contains $N$ different elements, each of them being shifted in phase by $2\pi\nu/N$. This sequence is used for $\gamma$-encoded homonuclear double-quantum recoupling. From \textsuperscript{29}.](image-url)
On the other hand, a $RN_n^\nu$ sequence consists in the concatenation of $N/2$ ($R_\phi R'_\phi$) elements with $\phi = \frac{\pi\nu}{N}$ spanning $n$ rotor periods, one R element being any pulses block which rotates the nuclear spins by $180^\circ$ around the x-axis. The symmetry number $N$ is always even.

Under the assumption of perfect heteronuclear decoupling, only the homonuclear interactions need to be taken into account. Figure 2.2 summarizes the relevant interactions and their rank which relates directly to their behaviour under spin- and space-rotation. Using the Magnus expansion of the effective Hamiltonian in the interaction frame:

$$\mathcal{H} = \mathcal{H}^{(1)} + \mathcal{H}^{(2)} + \mathcal{H}^{(3)} + \ldots,$$

(2.19)

where

$$\mathcal{H}^{(1)} = T^{-1} \int_{t_0}^{t_0+T} dt \tilde{H}(t)$$

(2.20)

$$\mathcal{H}^{(2)} = (2iT)^{-1} \int_{t_0}^{t_0+T} dt' \int_{t_0}^{t'} dt \left[ \tilde{H}(t'), \tilde{H}(t) \right]$$

(2.21)

with $t_0$ the starting time of the first C-element. The selection rules of the $CN_n^\nu$ sequences are derived as follows [45]:

$$\mathcal{H}^{\Lambda}_{lm\lambda\mu} = 0 \quad \text{if} \quad mn - \mu\nu \neq NZ \quad (2.22)$$

where $Z$ is any integer, whereas for the selection rules of the $RN_n^\nu$ sequences we find

$$\mathcal{H}^{\Lambda}_{lm\lambda\mu} = 0 \quad \text{if} \quad mn - \mu\nu \neq \frac{N}{2}Z\lambda \quad (2.23)$$

Figure 2.2: Homonuclear spin interactions in a solid rotating at the magic angle with respect to the external magnetic field, and their properties with respect to spatial and spin rotations. The spatial components with $m=0$ disappear for exact magic-angle spinning, in the case $l=2$. Adapted from [45].
where $Z_\lambda$ indicates any integer with the same parity as $\lambda$. Second order selection rules as well as selection rules for dual rotor-synchronised sequences can also be derived in a similar fashion (see [45]).

2.4. TOBSY Pulse Sequence

Throughout this work, we use the Total-Through Bond Correlation Spectroscopy (TOBSY) [35], where the polarization transfer is done via homonuclear J-couplings. This means all the other interactions appearing in the spin Hamiltonian must be suppressed to get an effective scalar Hamiltonian of the form:

\[ H_J = \sum_{i<j} 2\pi J_{i,j} \mathbf{I}_i \cdot \mathbf{I}_j \] (2.24)

In the following, we will assume the J-couplings to be fully isotropic, the anisotropy being completely averaged out by magic-angle spinning.

One of the first solid-state TOBSY pulse sequences was derived by Baldus and Meier using symmetry arguments [35] and can be written as $R_6^0$ and $R_8^0$ in the formalism of [29]. There is in fact an infinite number of such sequences which can be derived using average-Hamiltonian theory. Note that the symmetry-based theory tells nothing about the influence of the C or R basic elements on the performance of the sequence. Another problem is that this approach assumes perfect heteronuclear decoupling. As soon as interference effects between different channels begin to appear, the effective Hamiltonian derived is no longer valid and other terms appear leading to a worsening of the sequence.

Figure 2.3 depicts the pulse sequence used to assess experimentally the efficiency of the symmetry-based sequences. We start by a cross-polarization from the proton bath to the carbons. For that purpose, we use the adiabatic-passage Hartmann-Hahn cross polarization [46]. On the $^{13}$C-channel, we first generate a non-equilibrium polarization state described by the density operator $\sigma = I_\mathbf{z}_1$ using a 90° selective pulse on the spin 2 of a two-spins system. The coherences thus generated vanish away after the z-filter of duration $\tau_z$. The mixing block consists in the symmetry-based sequence $CN_n^\nu$ while decoupling on the proton channel. This decoupling is not specified yet. It is the subject of this work. Finally the FID is acquired after the last $\pi/2$ reading.
pulse under XiX-decoupling.

The transferred magnetisation to the second spin will show an oscillatory behaviour whose frequency should ideally equal the scalar coupling $J$ between the two spins. The C-Sequence is here a PC9$^1_6$ sequence where nine consecutive C-elements (here we use POST elements $(\pi/2)_{0^\circ}(2\pi)_{180^\circ}(3\pi/2)_{0^\circ}$), each phase-shifted by $2\pi/9$ with respect to the previous one, span 6 rotor periods.

2.5. Parameters used in Numerical Simulations

For all the numerical simulations carried out in Chapter 2 we used a four-spin system $C^2C^1H^1H^2$, i.e. a methylene group attached to a carbon. As shown in Table 2.1 to simulate 1,2-$^{13}$C-$^{15}$N-glycine-ethylester and 2,3-$^{13}$C-sodium propionate we use isotropic chemical shift of $\pm 8000$ Hz and $\pm 2100$ Hz respectively (typical for proton Larmor frequency of 500 MHz). If not stated otherwise, we use a powder averaging with 300 different crystallite orientations selected according to the Cheng-scheme.

2.6. Improving Polarization Transfer with an SC9 Sequence

In this section we study the influence of the C-sequence itself on the polarization transfer. We try to improve the polarization transfer by using a phase inversion supercycle which is implemented by forming SS’, where in the sequence S’ all the phases of the sequence S have been inverted (see Figure 2.5). It is known that such a supercycle cannot be used to construct a $\gamma$-encoded sequence, but since we generate an isotropic scalar Hamiltonian, this fact is irrelevant. We restrict ourselves to on-resonance CW-decoupling on the protons.

2.6.1. Experiment

The measurements have been carried out with a home-built 1.8 mm probe on a Varian Chemagnetics Infinity+ 500 spectrometer (11.4 T). The sample used was 1,2-$^{13}$C-$^{15}$N-glycine-ethylester. The pulse sequence is the same as the one depicted in Figure 2.3 but with the basic mixing blocks C9$^1_6$ replaced by SPC9$^1_6$ as shown in Figure 2.5. We used an MAS frequency $\nu_r$ of 20 kHz. The rf field intensity on the carbon channel $\nu_{1S}$ during the C-sequence was 60 kHz.
### Table 2.1.

Parameters of the four-spins system $C^2 \text{C}^1 \text{H}^1 \text{H}^2$ used in the GAMMA simulations. The dipolar strength $d$ is defined by Equation 2.9. The internuclear distance $r$ as well as the three Euler angles $\alpha$, $\beta$ and $\gamma$ are also given for each pair of nuclei. The J-couplings, and the isotropic chemical shifts are given in natural frequency units. To simulate glycine-ethylester we used the isotropic chemical shifts a) while b) was used for sodium propionate (typical for proton Larmor frequency of 500 MHz).

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<th>$r$ [Å]</th>
<th>$\alpha$ [°]</th>
<th>$\beta$ [°]</th>
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<td>-29</td>
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<tr>
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<table>
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<th>$\beta$ [°]</th>
<th>$\gamma$ [°]</th>
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<td>1200</td>
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<td>0</td>
<td>109</td>
<td>-146</td>
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</tbody>
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*Table 2.1.: Parameters of the four-spins system $C^2 C^1 H^1 H^2$ used in the GAMMA simulations. The dipolar strength $d$ is defined by Equation 2.9. The internuclear distance $r$ as well as the three Euler angles $\alpha$, $\beta$ and $\gamma$ are also given for each pair of nuclei. The J-couplings, and the isotropic chemical shifts are given in natural frequency units. To simulate glycine-ethylester we used the isotropic chemical shifts a) while b) was used for sodium propionate (typical for proton Larmor frequency of 500 MHz).*
Figure 2.3: Pulse sequence used to measure homonuclear through-bond polarization transfer. We start by APHH-cross polarization. Afterwards, a selective pulse, followed by a z-filter, generates an initial density operator $\sigma_0 = I_z$ for the two-spins system used. The mixing sequence consists of $k$ basic blocks. Each block contains 9 C-elements spanning 6 rotor periods. Each C-element is phase-shifted by $2\pi/9$ with respect to the previous one. One C-element is here a POST-element $(\pi/2)_{\theta},(2\pi)_{180^\circ},(3\pi/2)_{\theta}$. $k = 9$.
**Figure 2.4.** Graphical representation of the 4 spins-system $C^2C^1H^1H^2$ used in the GAMMA numerical simulations along with the internuclear distances. We used the same four-spins model system $C^2C^1H^1H^2$ to simulate $2,3^{13}C$-sodium propionate as well as $1,2^{13}C-^{15}N$-glycine-ethylester while adapting the chemical shifts (see Table 2.1).

$$\begin{align*}
\text{a)} \\
&C_{96}^1 \\
&\begin{pmatrix}
\phi=0 & 2\pi/9 & 4\pi/9 & 6\pi/9 & 8\pi/9 & 10\pi/9 & 12\pi/9 & 14\pi/9 & 16\pi/9 \\
\tau_r & & & & & & & & \\
\end{pmatrix} \\
\text{b)} \\
&SC_{12}^1=C_{96}^1C_{96}^{-1} \\
&\begin{pmatrix}
\phi=0 & 2\pi/9 & 4\pi/9 & 6\pi/9 & 8\pi/9 & 10\pi/9 & 12\pi/9 & 14\pi/9 & 16\pi/9 \\
\tau_r & & & & & & & & \\
\end{pmatrix}
\end{align*}$$

**Figure 2.5.** a) Building block of the $C_{96}^1$ sequence and b) its phase inversion supercycled counterpart $SC9$. Note that the MAS frequency stays the same for both sequences. As a C-element we used a POST-element $(\pi/2)_{0^0}(2\pi)_{180^0}(3\pi/2)_{0^0}$.
2.6.2. Results

Experiment

In Figure 2.6a) we show the experimental polarization transfer from spin 1 (CO) to spin 2 (Cα) for the sequence PC9\textsuperscript{16} and using a fixed decoupling rf-field intensity \( \nu_1 I \) of 197 kHz. Figure 2.6b) depicts the same polarization transfer when using the supercycled version PSC9\textsuperscript{16}, keeping all the other experimental parameters constant. Note that the use of the supercycled version means that we have a cycle time twice as long as the one for PC9\textsuperscript{16} and consequently twice as less data points. We note that the sum polarization decay is about the same for both PC9\textsuperscript{16} and PSC9\textsuperscript{16}. This means basically that the mechanism responsible for this decay is unaffected by the supercycle and is probably of heteronuclear origin (between protons and carbons). On the other hand, we obtain about 10% more transferred polarization in the case of the supercycled version at the position of the first maximum (\( t_{\text{mix}} = 7.2 \text{ ms} \)). Indeed, such supercycles are known to suppress a large number of cross-terms causing interferences between dipole-dipole couplings and chemical shift anisotropies\[50\]. Figure 2.6c) and Figure 2.6d) show the decoupling rf-field intensity dependence of the polarization transfer for a fixed mixing time \( t_{\text{mix}} \) of 7.2 ms for PC9\textsuperscript{16} and PSC9\textsuperscript{16} respectively, showing again the 10% enhanced polarization transfer for the supercycled version.

Simulation

The enhanced polarization transfer using the supercycled version of PC9 could be confirmed by a numerical simulation using GAMMA\[37\]. Taking a four-spin system \( C^1C^2H^1H^2 \) with the parameters given in Table 2.1(a), we simulated a polarization transfer \( S_{z1} \rightarrow S_{z2} \) starting from \( \sigma_0 = S_{z1} \) (\( S_2 \) is here the methylene carbon). Figure 2.8a) shows transferred polarization from spin 1 to spin 2 as a function of the decoupling rf-field intensity \( \nu_1 I \) and the mixing time \( t_{\text{mix}} \) using the PC9\textsuperscript{16} sequence. Figure 2.8b) shows the same polarization transfer in the case of the supercycled sequence PSC9\textsuperscript{16}. Figure 2.8c) compares the polarization transfer obtain with both sequences PC9\textsuperscript{16} and PSC9\textsuperscript{16} for a fixed decoupling rf-field intensity \( \nu_1 I \) of 197 kHz as a function of mixing time. We observe a maximum polarization transfer of about 57% at \( t_{\text{mix}} = 9.6 \text{ ms} \) in the case of PC9\textsuperscript{16} compared to a maximum of about 67% transferred polarization at a mixing time \( t_{\text{mix}} = 9.8 \text{ ms} \) using PSC9\textsuperscript{16}. Thus, we get about 10% more transfer in the latter case and this 10% improvement is in agreement with the measurements of Figure 2.6. Finally, in Figure 2.8d)
2.6 Improving Polarization Transfer with an SC9 Sequence

Figure 2.6.: Experimental transfer as a function of mixing-time for a fixed decoupling-field intensity $\nu_{1I} = 197 \text{ kHz}$ for a)PC$_{916}$ and b)PSC$_{916}$. Experimental transfer as a function of the decoupling-field intensity for a fixed mixing-time $t_{\text{mix}}=7.2 \text{ ms}$ for c)PC$_{916}$ and d)PSC$_{916}$. The sample used was 1,2-$^{13}\text{C}$-$^{15}\text{N}$-glycine-ethylester. The MAS spinning frequency $\nu_r$ was set to 20 kHz and the rf field intensity $\nu_{1S}=60 \text{ kHz}$. The measurements were carried out with a home-built 1.8 mm probe on a Varian Chemagnetics Infinity+ 500 spectrometer(11.4T)[49]. The green triangles show the sum polarization.
we plot slices out of Figure 2.8a) and Figure 2.8b) showing the transferred polarization $<S_{2z}>$ as a function of the decoupling rf-field intensity for a constant mixing time $t_{\text{mix}}=9.6\ \text{ms}$. As can be seen, the GAMMA simulation is also able to reproduce the 10% polarization transfer enhancement of the PSC9\textsuperscript{1} over the PC9\textsuperscript{1} sequence as in Figure 2.6d). Note that we also observe about twice as many resonance conditions in the case of the supercycled sequence PSC9\textsuperscript{1}, its cycle time being twice as long as the one as the one of PC9\textsuperscript{1}. The strongest resonance conditions shown in Figure 2.6 at $\nu_{1H} = 180\ \text{kHz}$ and $\nu_{1H} = 213\ \text{kHz}$ are also reproduced in Figure 2.8 although the second one being a little shifted (218 kHz).

**Conclusion**

To conclude, we have demonstrated experimentally and numerically that a supercycled version PSC9\textsuperscript{1} was able to lead a 10% enhanced polarization transfer compared to the standard PC9\textsuperscript{1} sequence. While we used on-resonance CW-decoupling it may be interested to try other heteronuclear decoupling, for instance off-resonance CW-decoupling as in Section 3.5 or XiX-decoupling as in Section 2.7. We think this point deserves further research.
2.6 Improving Polarization Transfer with an SC9 Sequence

Figure 2.8: Simulated transfer as a function of mixing-time and rf decoupling intensity (steps of 250Hz) for a) a POST-C9 sequence and b) a POST-SC9 sequence. c) Transferred polarization for both sequences PC9 and PSC9 as a function of the mixing-time for a constant decoupling-field intensity $\nu_{1I}=197$ kHz. d) Simulated transferred polarization at a constant mixing-time of $t_{mix}=9.6$ ms as a function of the decoupling-field intensity. We used a four-spin system $C^4 C^2 H^1 H^2$ (see Section 2.5) modeling glycine-ethylester at a proton Larmor frequency of 500 MHz. We used $\nu_r=20$ kHz and $\nu_{1S}=60$ kHz. The simulation also reproduces the strong resonance condition at $\nu_{1I}=180$ kHz, and the one at $\nu_{1I}=218$ kHz (although experimentally around $\nu_{1H}=213$ kHz), whereas the smaller one are not observed experimentally. We also observe about twice as many resonance conditions for the supercycled sequence, its cycle time twice as long.
2.7. XiX-decoupling during PC9

The standard $^1$H-decoupling during C-sequences has been a strong off-resonance irradiation which is known to give good results\cite{35,51} (experimentally, Hardy et al.\cite{52} found a proton decoupling rf offset of 190 kHz for a decoupling rf field intensity of 160 kHz). The decoupling effective field should be as strong as possible in order to avoid unwanted higher order Hartmann-Hahn recoupling conditions between carbons and protons.

In this chapter we study the use of on resonance XiX-decoupling on the proton channel while applying the PC9$^6$ on the $^{13}$C channel. The pulse sequence is again the one shown in Figure 2.3, the decoupling on the proton channel being now, as for the detection period, XiX-decoupling. The experimental work presented in Section 2.7 was carried out together with Ingo Scholz.

2.7.1. Experiment

The measurements have been carried out with a home-built 1.8 mm probe on a Varian Chemagnetics Infinity+ 500 spectrometer(11.4T)\cite{49}. The samples used were 1,2-$^{13}$C-$^{15}$N-glycine-ethylester and 2,3-$^{13}$C-sodium propionate.

2.7.2. Results

Figure 2.9a) shows the experimental transfer as a function of the XiX-modulation frequency $\nu_{m,XiX}$ and the decoupling-field intensity $\nu_{I1}$ for 2,3-$^{13}$C-sodium propionate. The magic-angle spinning frequency $\nu_r$ was set to 20 kHz. This was one of the first tries of using XiX as proton decoupling scheme where we started by expressing the modulation frequency $\nu_{m,XiX}$ as a multiple of the MAS frequency $\nu_r$. The range of the ratio $\nu_{m,XiX}/\nu_r$ was chosen from 0.4 to 1.7 corresponding to XiX-modulation frequencies from 8 to 34 kHz. We see here two conditions where the transfer is markedly more pronounced, one at $\nu_{m,XiX}/\nu_r = 0.75$ and one at $\nu_{m,XiX}/\nu_r = 1$. It should be noticed that the decoupling-field intensity is quite high (from 190 kHz to 230 kHz), the transfer being much less at lower field intensity (data not shown).

Figure 2.9b) depicts the simulated polarization transfer in the case of a four-spins system $^{12}$C$^1$H$^1$H$^2$ whose parameters are given in Table 2.1 for the same conditions as the measurements. The simulation reproduces quite well the good decoupling conditions at $\nu_{m,XiX}/\nu_r = 0.75$ and $\nu_{m,XiX}/\nu_r = 1$. There is a condition around $\nu_{m,XiX}/\nu_r = 0.6$ which is found in the simu-
Figure 2.9.: transferred polarization (CH\textsubscript{3}) as a function of the XiX-modulation frequency $\nu_{m,XiX}/\nu_r$ and decoupling field intensity $\nu_{1I}$. a) experimental transfer CH\textsubscript{2} $\rightarrow$ CH\textsubscript{3} for 2,3-$^{13}$C-sodium propionate using PC\textsubscript{9} and XiX decoupling on the protons and with $\nu_r = 20$ kHz. The rf-amplitude on the carbon channel was set to $\nu_{1S} = 60$ kHz while the mixing-time $t_{mix}$ was 9 ms. The measurements were performed on a Varian Infinity+ 500 MHz spectrometer using a 1.8 mm MAS probe\textsuperscript{[49]} (Experiment done together with Ingo Scholz). b) GAMMA\textsuperscript{[37]} simulation using a four-spin system $C^2C^3H^1H^2$ with the parameters described in Table 2.1.
Decoupling during TOBSY Sequences

Decoupling but not as clearly in the experimental plot. There is also a small region on the band \( \nu_{m,\Xi X}/\nu_t = 0.75 \) around \( \nu_1 = 209 \text{kHz} \) where no transfer is observed in the simulation whereas a good transfer is observed in the experiment. The origin of these discrepancies is unclear.

Figure 2.10 compares CW-decoupling with XiX-decoupling using \( \nu_{m,\Xi X}/\nu_t = 1 \). Figure 2.10a) and Figure 2.10c) show the mixing-time dependence of the transfer, while b) and d) depict the decoupling-field intensity dependence. Here the MAS frequency \( \nu_t \) was set to 30 kHz. From Figure 2.10a) and Figure 2.10c), it is apparent that for longer mixing-times, the oscillation is damped less rapidly for \( \nu_{m,\Xi X}/\nu_t = 1 \) than for CW-decoupling. Another strong point in favor of \( \nu_{m,\Xi X}/\nu_t = 1 \) is the much smoother behaviour of the field intensity dependence (see Figure 2.10d)) compared to the much irregular field-dependence for CW-decoupling (see Figure 2.10b)). Practically this means a gain of time because the optimisation needed for CW-decoupling to avoid resonance conditions is no longer needed.

Figure 2.11a) shows this time the dependence of the transferred polarization on the XiX-modulation frequency \( \nu_{m,\Xi X} \) and on the decoupling-field intensity of \( 1,2^{-13}\text{C,}^{15}\text{N-glycineethyl-} \) ester measured at a MAS frequency \( \nu_t \) of 25 kHz. The decoupling-field intensity range was here much broader than the one in Figure 2.9 i.e. from 30 kHz to 200 kHz. Moreover, the range of the ratio \( \nu_{m,\Xi X}/\nu_t \) was also increased from 0.6 to 4, giving XiX-modulation frequencies \( \nu_{m,\Xi X} \) from 10 to 100 kHz. We see here a new good decoupling condition appearing at 75 kHz corresponding to \( \nu_{m,\Xi X} = \nu_{1S} \) or \( \nu_{m,\Xi X}/\nu_t = 3 \) for a PC9\textsubscript{16} sequence, where the transfer stays quite high also at lower field intensity. The condition at \( \nu_{m,\Xi X} = \nu_t \) is still visible but not as strong as the new discovered one. There is also some transfer around \( \nu_{m,\Xi X} = 37 \text{kHz} \) which corresponds probably to \( \nu_{m,\Xi X} = \nu_{1S}/2 \). Again, a GAMMA\textsuperscript{37} simulation using parameters of Table 2.1(a) was able to reproduce the salient features of the experimental measurement, especially the condition \( \nu_{m,\Xi X} = \nu_{1S} \). The simulation is shown in Figure 2.11b).

In Figure 2.12 we show the normalized transferred polarization for the three decoupling schemes used, a) \( \nu_{m,\Xi X} = \nu_t \), b) \( \nu_{m,\Xi X} = \nu_{1S} \) and c) CW-decoupling. To check if the observed transfer at low decoupling-field intensity for the condition \( \nu_{m,\Xi X} = \nu_{1S} \) is indeed a scalar transfer through the C-C bond, we performed a simulation where this coupling \( J_{\text{CC}} \) was set to zero (shown on
shown in Figure 2.13 shows the decoupling-field amplitude dependence of the normalized polarization transfer. The curves are vertical slices out of the four contour plots of Figure 2.12 at a fixed mixing-time of $t_{\text{mix}} = 9\,\text{ms}$. To reduce the many resonance conditions of the CW-decoupling the curves have been convoluted with a 2% rf inhomogeneity. The curve in red, which is a slice out at $t_{\text{mix}} = 9\,\text{ms}$ out of Figure 2.12d), shows a simulation where the scalar coupling $J_{\text{CC}}$ has been set to zero. The transfer thus observed is due to residual dipolar couplings which are not fully averaged out by the sequence and the magic angle spinning. As is seen from the figure, for a decoupling-field intensity of about 160 kHz, there is a maximum of $\sim 25\%$ polarization transferred due to residual dipolar couplings.

Finally, we may tentatively provide an explanation as to why the XiX-decoupling condition with $\nu_{m,\text{XiX}} = \nu_{1S}$ works so well. If we look at the transferred polarization curve of Figure 2.13 when CW-decoupling is used on protons, we notice a small local maximum amounting to a transfer of about 19% when the decoupling field intensity $\nu_{1I}$ is set to 75 kHz. It is probably the reduced number of resonance conditions for that specific field intensity (denoted by the dashed line on Figure 2.13) which leads the enhanced polarization transfer. We may argue that for XiX-decoupling with $\nu_{m,\text{XiX}} = \nu_{1S}$, it is the XiX-modulation frequency which plays the role of the CW-nutation field intensity $\nu_{1I,CW}$ leaving the field intensity of the XiX-decoupling scheme $\nu_{1I,\text{XiX}}$ as free parameter, upon which the decoupling efficiency is directly proportional.

### 2.7.3. Conclusion

Thus, when replacing CW-decoupling with an XiX-decoupling on the protons, while applying in the TOBSY sequence PC9 on carbons, we have found interesting decoupling conditions when the modulation frequency $\nu_{m,\text{XiX}} = \nu_{t}$ or $\nu_{m,\text{XiX}} = \nu_{1S}$. Both XiX-decoupling schemes present a much smoother behaviour with respect to the decoupling rf-field intensity compared to CW decoupling (see Figure 2.13). Furthermore, the XiX-decoupling scheme with $\nu_{m,\text{XiX}} = \nu_{1S}$ exhibit an improved transfer compared to CW-decoupling over the whole range $0\,\text{kHz} \leq \nu_{1I} \leq 500\,\text{kHz}$ (see Figure 2.12 and Figure 2.13).
2.8. Generalisation of XiX to Dual-Channel Symmetry-based Sequences $PC_9^1CN_6^\nu$

First, the good decoupling condition $\nu_{m,XiX} = \nu_{1S} = 3\nu_r$ on protons while the sequence $PC_9^1$ is applied on carbons can be expressed as a dual rotor-synchronized symmetry-based sequence of the form $PC_9^1LiL180^0$. The basic C-element of the protons decoupling sequence is now the concatenation of two rectangular pulses with arbitrary flip angles, the second one being $\pi$-phase-shifted with respect to the first one. In the following, we denote one such pulse as “L” leading to the C-element L-inverse-L or in shorthand notation LiL. The rectangular pulse L of arbitrary flip-angle is characterized by its duration, derived from the sequence symmetry and its intensity which is in our case the decoupling-field intensity $\nu_{1I}$. By analysing now the general sequence $C9^1C180^0$ with the Mathematica package of Levitt[36] we find 11 first-order symmetry-allowed terms. In this case, we note that the symmetry number $\nu$ in the sequence $PC_9^1CN_6^\nu$ equals zero, meaning we don’t have z-rotation for the symmetry-based sequence on protons $C180^0$. In Subsection 2.8.1 we set the symmetry number $\nu$ to zero and varied the symmetry number $N$ from 0 to 100 and selected only sequences giving the minimum number of symmetry-allowed terms (in first order). We obtained 10 sequences which are listed in Table 2.2. Note that the sequences so derived are valid for any arbitrary C-element and not necessarily for C-elements of the form LiL. For instance, if we would choose a rectangular pulse with a flip angle $2\pi$, we would simply get degenerate sequences, all corresponding to CW-decoupling. Despite the freedom we have in choosing the C-elements, we will nevertheless use $C\equiv LiL$ when numerically assessing the derived sequences listed in Table 2.2 with GAMMA[37]. The effect of setting the symmetry number $\nu$ to zero when $C\equiv LiL$ means basically that we restrict the proton decoupling sequences to XiX-decoupling with the XiX-modulation frequency $\nu_{m,XiX}$ directly proportional to the symmetry number $N$. The results of the numerical simulations on a four-spin system (see Section 2.5) will be presented in Subsection 2.8.1.

Second, by setting the symmetry number $\nu$ in sequences $PC_9^1CN_6^\nu$ to values different from zero (i.e. meaning $\nu \neq 0$), we obtain sequences with $z$-rotations. Although it is not possible anymore to express the good XiX-decoupling condition $\nu_{m,XiX} = \nu_{1S} = 3\nu_r$ without $z$-rotation, we obtain a reduced minimum number of symmetry-allowed terms from 11 to 7. Consequently,
we again screened the sequences PC$9^1_6$CN$^\nu_6$ by varying the symmetry numbers $N$ and $\nu$ in the range $1 < N < 100$ and $1 < \nu < N$. Indeed, by the definition of the phase-shift $2\pi \cdot \nu/N$, we have the restriction $\nu \leq N$ to avoid redundant sequences. For instance, the sequence PC$9^1_6$C$9^1_6$ is equivalent to PC$9^1_6$C$9^1_6^{10}$ as they both have a z-rotation phase shift increments of 40°. We obtained 185 dual-channel symmetry-based sequences with z-rotation over the specified range of symmetry numbers $N$ and $\nu$. Those sequences are listed in Table 2.3 of Subsection 2.8.2. Again the symmetry-based sequences derived are valid for any C-elements. Note that this time, due to the z-rotation ($\nu \neq 0$), a sequence whose basic C-element is a $2\pi$ rectangular pulse doesn’t correspond to CW-decoupling any more. As in the case of sequences without z-rotation, we choose as a C-element the block LiL meaning again the concatenation of the rectangular pulses, the second one being $\pi$-phase-shifted with respect to the first one. In Subsection 2.8.2 we use the 185 derived sequences and check numerically their efficiency using a TOBSY polarization transfer scheme in the GAMMA$^{[37]}$ environment and the parameters given in Table 2.1(a).

Third, if we use a rectangular pulse with arbitrary flip-angle $L$ instead of a C-element, we can also express the condition $\nu_{m,XiX} = \nu_{1S} = 3\nu_t$ as PC$9^1_6$L$36_6^{18}$. In the following, we will call dual-channel symmetry-based sequences of the form PC$9^1_6$LN$^\nu_n$ $L$-sequences. Although we know from the beginning that the C-theory doesn’t apply with an L- instead of a C-sequence, we nevertheless simulated the 185 L-sequences with the symmetry numbers $N$, $n$ and $\nu$ listed in Table 2.3 with GAMMA$^{[37]}$ and compared their efficiency (see Subsection 2.8.3). Note that L-sequences without z-rotation are all equivalent to CW-decoupling and have therefore not been simulated.

The terms associated with an interaction $\Lambda$, are characterized by their space-rank $l$ and their $2l + 1$ space-components $m$ running from $-l$ to $+l$, as well as their spin-rank $\lambda$ and their $2\lambda + 1$ spin-components $\mu$ running from $-\lambda$ to $+\lambda$. In the Mathematica package$^{[36]}$, for a dual-channel sequence involving spins $S(\text{C}^{13})$ and spins $I(\text{H}^1)$, the terms are expressed as:

\[
\{\{\Lambda, O\}, \{l, m\}, \{\lambda_S, \mu_S\}, \{\lambda_I, \mu_I\}\}\tag{2.25}
\]

with $\Lambda = \{\text{isoCS, CSA, J, DD or rf}\}$, and $O = \{S, SS, I, II \text{ or IS}\}$ depending on the interaction. It has indeed been shown that the effect of rf-inhomogeneity (denoted here “rf”) can be implemented as a selection rule in the context of symmetry-based sequences (see Chapter 2.17 in$^{[29]}$).
To summarize, in the three following Subsections we will assess numerically dual-rotor synchronized symmetry-based TOBSY sequences of the type PC9\(1_{6}^{1}\)LiLN\(\nu_{n}=0\) (Subsection 2.8.1), PC9\(1_{6}^{1}\)LiLN\(\nu_{n} \neq 0\) (Subsection 2.8.2) and PC9\(9_{6}^{1}\)LN\(\nu_{n} \neq 0\) (Subsection 2.8.3). For each sequence, we will study the polarization transferred to spin C\(2\) from spin C\(1\) in a four spin system C\(2\)C\(1\)H\(1\)H\(2\) (see Table 2.1) as a function of the decoupling field intensity \(\nu_{1I}\) and mixing time \(t_{mix}\) and finally compare their efficiency at a constant mixing-time \(t_{mix}\) as a function of \(\nu_{1I}\).

### 2.8.1. C-Sequences Decoupling without z-Rotation

In this case, using the Mathematica package of Levitt\cite{36}, we select only C-sequences of the form PC9\(9_{6}^{1}\)CN\(\nu_{n}=0\), setting \(\nu\) to zero, giving the minimum number of 11 first-order symmetry-allowed terms:

\[
\{\{\text{isoCS}, \text{S}\}, \{0, 0\}, \{1, 0\}, \{0, 0\}\}, \{\{\text{isoCS}, \text{I}\}, \{0, 0\}, \{0, 0\}, \{1, 1\}\},
\{\{\text{J}, \text{SS}\}, \{0, 0\}, \{0, 0\}, \{1, 1\}\}, \{\{\text{J}, \text{SI}\}, \{0, 0\}, \{1, 0\}, \{1, -1\}\},
\{\{\text{rf}, \text{I}\}, \{0, 0\}, \{0, 0\}, \{1, 1\}\}\}
\]

In particular, we note the presence of two “rf” inhomogeneity terms and two terms associated with isotropic chemical shifts on the I channel (protons) which are absent on the S channel (carbons). We will see in Subsection 2.8.2 that the use of z-rotations will remove those four terms. In the subsequent Figures, we show only results where the transferred polarization was higher than CW-decoupling over the decoupling-field intensity range from 0 to 160 kHz. Indeed, finding a good decoupling scheme at low-power is strongly desirable, especially in the context of protein-solid-state NMR where a too strong rf intensity can damage the sample. From now on, we use the notation [\(N n \nu\)] to refer to a specific sequence PC9\(9_{6}^{1}\)CN\(\nu\).

In Figure 2.14, we first note that the transfer without decoupling (i.e. \(\nu_{1I} = 0\) kHz) amounts to about 16%, a quite low transfer meaning that proton decoupling is mandatory in this case (\(\nu_{I} = 20\) kHz) to obtain a reasonable transfer. We then notice that one specific problem of CW-decoupling is the noticeable transfer decrease in the range \(\nu_{1I} \leq 160\) kHz, which makes them
2.8 Generalisation of XiX to Dual-Channel Symmetry-based Sequences PC9\textsubscript{1} \text{CN}_6\textsuperscript{v=0}

hardly applicable for protein-NMR spectroscopy. We recognise the sequence [18 6 0] as the condition \( \nu_{m,\text{XiX}} = \nu_{1S} \) or \( \nu_{m,\text{XiX}}/\nu_r = 3 \) from Figure 2.13 with its much higher transferred polarization compared to CW-decoupling. The three other sequences [36 6 0], [45 6 0] and [54 6 0], which are also XiX-decoupling with modulation frequencies of \( \nu_{m,\text{XiX}} = 2 \nu_{1S}, \nu_{m,\text{XiX}} = 2.5 \nu_{1S} \) and \( \nu_{m,\text{XiX}} = 3 \nu_{1S} \) respectively, exhibit also a better transfer over the low-field region \( \nu_{1I} \leq 160 \text{ kHz} \) compared to CW-decoupling. Their efficiency in the range \( 0 \leq \nu_{1I} \leq 160 \text{ kHz} \) seems to lower when the symmetry number \( N \) is increased. On the other hand, if high-power decoupling would be available (i.e. \( \nu_{1I} \geq 250 \text{ kHz} \)), we note that the sequence [36 6 0] (in other words XiX-decoupling with \( \nu_{m,\text{XiX}} = 2 \nu_{1S} \)) would lead to an even higher transferred polarization than [18 6 0] reaching up to 85\% transferred polarization above \( \nu_{1I} = 300 \text{ kHz} \) compared to about 75\% for [18 6 0].

Interestingly, we note in Figure 2.15 that as soon as \( N \) gets larger, here \( N = 63, 72, 81 \) and 90, corresponding to \( \nu_{m,\text{XiX}} = 3.5 \nu_{1S}, 4 \nu_{1S}, 4.5 \nu_{1S} \) and \( 5 \nu_{1S} \) respectively, one reaches a kind of asymptotic behaviour for the transferred polarization in the low-field range \( \nu_{1I} \leq 160 \text{ kHz} \) which seems to converge to the value of the transfer without decoupling (i.e. \( \nu_{1I} = 0 \)). This fact shows that a higher XiX-modulation frequency do not necessarily improve the efficient of the decoupling.

Overall, out of the ten dual-channel decoupling sequences (listed in Table 2.2) tested, eight outperformed CW-decoupling over the decoupling field intensity range \( \nu_{1I} \leq 160 \text{ kHz} \). On the other hand, we find that the best sequence is [18 6 0] which is nothing else than XiX-decoupling with \( \nu_{m,\text{XiX}} = \nu_{1S} \). The sequence [36 6 0] is the second best one and for decoupling field intensities

| \( N \) | 9,18,27,36,45,54,  
| --- | 63,72,81,90  |
| \( n \) | 6 |
| \( v \) | 0 |

Table 2.2.: List of the 10 different dual-channel C-sequences of the form PC9\textsubscript{1} \text{CN}_6\textsuperscript{v=0} without z-rotation on the proton channel which were numerically tested in this work.
above 250 kHz leads to an even higher transfer than [18 6 0] and could be the method of choice if very high decoupling-field intensities are at hand.

2.8.2. C-Sequences Decoupling with z-Rotation

In this case, using the Mathematica package of Levitt\cite{36}, we select only TOBSY sequences with z-rotation of the form PC9\textsuperscript{1}CN\textsuperscript{\nu}_n \neq 0 giving the minimum number of 7 first-order symmetry-allowed terms. There are four terms less associated with the rf inhomogeneity and the isotropic chemical shift on the I-channel (\textsuperscript{1}H channel) compared to what was derived in Subsection 2.8.1. The symmetry-allowed terms are:

\begin{align*}
\{\{\text{isoCS}, S\}, \{0, 0\}, \{1, 0\}, \{0, 0\}\}, \{\{\text{isoCS}, I\}, \{0, 0\}, \{0, 0\}, \{1, 0\}\}, \\
\{\{J, SS\}, \{0, 0\}, \{0, 0\}, \{0, 0\}\}, \{\{J, SI\}, \{0, 0\}, \{1, -1\}, \{1, 1\}\}, \\
\{\{J, SI\}, \{0, 0\}, \{1, 0\}, \{1, 0\}\}, \{\{J, SI\}, \{0, 0\}, \{1, 1\}, \{1, -1\}\}, \\
\{\{J, II\}, \{0, 0\}, \{0, 0\}, \{0, 0\}\}\}
\end{align*}

We show again only sequences leading to a larger polarization transfer than CW-decoupling for decoupling field intensities on the range 0 to 160 kHz. One important point is to note that PC9\textsuperscript{1}CN\textsuperscript{\nu}_n and PC9\textsuperscript{1}CN\textsuperscript{N-\nu}_n differ only in the sense of rotation of the z-rotation. We expect the performance of both sequences to be quite similar. Indeed, as has been shown by Eden and Levitt\cite{44}, the number of symmetry-allowed terms is insensitive to the sign of \nu. For instance, in Figure 2.16, the transferred polarization for [18 6 1] is very similar to [18 6 17], or [27 6 9] is very similar to [27 6 18] in Figure 2.17. In the following, we will refer to the sequence PC9\textsuperscript{1}CN\textsuperscript{N-\nu}_n as the “minus-\nu” counterpart of the PC9\textsuperscript{1}CN\textsuperscript{\nu}_n sequence.

The best sequences with z-rotation shown in Figure 2.16\textsuperscript{e}) are the [18 6 1] and [18 6 17] which exhibit a maximum transferred polarization of about 55% at \nu = 160 kHz but are as bad as CW-decoupling for \nu \leq 160 kHz. The [18 6 9] sequence doesn’t seem to have this behaviour on that decoupling-field intensity range over which it outperforms CW-decoupling but shows strange oscillations as the field intensity increases and is much less efficient than CW-decoupling for \nu \geq 150 kHz.

In Figure 2.17, sequences [27 6 9], [27 6 18] and [36 6 27] still exhibit the reduced transfer for \nu \leq 140 kHz. This is in contrast to [36 6 18], where we find a little higher polariza-
The three sequences shown in Figure 2.18 with the symmetry number $N=54$ do not show the decreased transfer for decoupling-field intensity $\nu_{11}$ below 160 kHz, but they seem to be bounded to less than 30% on this range. The sequence $[54 \ 6 \ 27]$ again exhibits a strange oscillation in the region $\nu_{11} \geq 200$ kHz, similar to the one observed for $[18 \ 6 \ 9]$ (see Figure 2.16b and e)).

Figure 2.19 demonstrates again the asymptotic behaviour of the transferred polarization as $N$ gets larger. The limiting value is again the transferred polarization of about 16% obtained without decoupling (i.e. with $\nu_{11} = 0$). We note also that the influence of the symmetry number $\nu$ seems less marked, as the polarization curves with different $\nu$ show a similar behaviour.

Finally, we may say that from the 185 sequences tested using z-rotation (listed in Table 2.3), we found only 14 sequences (depicted in Figure 2.16 to Figure 2.19) having a higher polarization transfer in the range $\nu_{11} \leq 160$ kHz. However the polarization transfer, seems to be bounded the the maximum polarization transfer of 50% attained by sequences $[18 \ 6 \ 1]$ and $[18 \ 6 \ 7]$ at $\nu_{11}=160$ kHz, all the other sequences leading to a lower polarization transfer. To conclude, we may say that although the selected C-sequences with z-rotations outperform CW-decoupling in the rf-field intensity range $0 \leq \nu_{11} \leq 160$ kHz, and exhibit much less resonance conditions, the obtained polarization transfer seem too low for practical application. Moreover, as already noted before, it is not possible to express the good XiX-decoupling condition $\nu_{m,XiX}=\nu_{1S}$ using TOBSY sequences of the type $\text{PC9}_{16}^L\text{LiLN}_n$, i.e. with z-rotation.

### 2.8.3. L-Sequences Decoupling with z-Rotation

The decoupling scheme XiX with $\nu_{m,XiX}=\nu_{1S}$ can also be written as $\text{PC9}_{16}^L\text{LiLN}_n^\nu$, where L represents a rectangular pulse with arbitrary flip angle. As already explained in the beginning of this section, those L-elements are no longer multiples of 360° rotations (including zero), meaning
the C-sequence theory doesn’t apply any more. Nevertheless, because the condition $\nu_{m,XiX} = \nu_{1S}$ can be expressed in such a fashion, we tried again the 185 L-sequences with the symmetry numbers $N \ n$ and $\nu$ given in Table 2.3 and looked for possible high-efficiency decoupling sequences. Similar to what was done in Subsection 2.8.1 and Subsection 2.8.2, we studied numerically with GAMMA^37 the polarization transfer in a four-spin systems as a function of mixing time and decoupling field intensity $\nu_{1I}$. The results are depicted in Figure 2.20 to Figure 2.22. For a sequence $PC9_6LN^\nu_n$ we use the shorthand notation $L[N \ n \ \nu]$.

We show again only sequences leading to a larger polarization transfer than CW-decoupling for decoupling-field intensities $\nu_{1I}$ in the range 0 to 160 kHz. Sequence $L[18 \ 6 \ 9]$ in Figure 2.20 shows a better transfer for $\nu_{1I} \leq 160$ kHz but again strange oscillations when $\nu_{1I}$ increases similar to the ones appearing with the sequence $[54 \ 6 \ 27]$ in Figure 2.18(b) and $[18 \ 6 \ 9]$ in Figure 2.16(b). On the other hand, sequence $L[18 \ 6 \ 8]$ and its minus-$\nu$ counterpart $L[18 \ 6 \ 10]$ show a much lower transferred polarization for $\nu_{1I} \leq 160$ kHz, similar to CW-decoupling. For a decoupling-field intensity larger than 160 kHz, the transferred polarization is much higher, reaching 85% at about $\nu_{1I} = 165$ kHz which is even higher than the 60% of the condition $\nu_{m,XiX} = \nu_{1S}$ for the

<table>
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Table 2.3.: List of the 185 different dual-channel C-sequences of the form $PC9_6LN^\nu_n$ without z-rotation (meaning $\nu \neq 0$) on the proton channel which were numerically tested in this work.
same decoupling-field intensity. Thus, if decoupling field intensities $\nu_{1I}$ higher than 160 kHz are available, we expect both sequences L[18 6 8] and L[18 6 10] to be relevant for practical applications.

In Figure 2.21, we recognise again that the sequence L[36 6 18] is fully equivalent to the condition $\nu_{m,\text{XiX}} = \nu_{1S}$. Besides, we show two very interesting decoupling sequences, L[36 6 17] and its minus-$\nu$ counterpart L[36 6 19] for which the transfer in the lower region $\nu_{1I} \leq 160$ kHz is better than CW-decoupling, while they reach a transfer as high as 80% for $\nu_{1I} = 160$ kHz which is much above the 55% of CW-decoupling and even higher than the 65% of the very efficient L[36 6 18] sequence. Again, for application where decoupling field intensities $\nu_{1I}$ higher than 160 kHz are at hand, we may recommend sequences L[36 6 17] or L[36 6 19] as method of choice for proton decoupling when the PC9 is applied on the carbons.

Finally, we show three sequences with the symmetry number $N=72$ in Figure 2.22. The sequence L[72 6 36] corresponds again to the condition $\nu_{m,\text{XiX}} = 2 \nu_{1S}$ (as sequence [36 6 0] in Figure 2.14b)). The sequences L[72 6 35] and its minus-$\nu$ counterpart L[72 6 37] show again a better transfer for the low-field region $\nu_{1I} \leq 160$ kHz compared to CW-decoupling. Nevertheless, the efficiencies of the three sequences depicted in Figure 2.22 do not much outperform the one of CW-decoupling and are not foreseen to have practical relevance. As already discussed in Subsection 2.8.1, we can again conclude that increase the symmetry number $N$ do not necessarily improves the efficiency of the decoupling sequences.

To conclude, out of the 185 L-sequences with $z$-rotation tested, we found 9 sequences leading to significantly better polarization transfer in the range 0 to 160 kHz. Apart from the known good decoupling condition $\nu_{m,\text{XiX}} = \nu_{1S}$ which could be expressed this time as L[36 6 18], we found four sequences leading to transfers similar or higher than this latter, namely L[18 6 8] and L[36 6 17] with their minus-$\nu$ counterparts L[18 6 10] and L[36 6 19] respectively. Those four sequences are expected to work best when decoupling field intensities $\nu_{1I}$ higher than 160 kHz are available. For instance, L[36 6 17] can lead to a polarization transfer up to 85% for a decoupling field intensity of 180 kHz, which is about 20% more than the 65% of the L[36 6 18] for the same field intensity.
2.9. Conclusion

We first showed in Section 2.6 experimentally that a phase inversion supercycled version \( \text{PSC9}_6^1 \) of a \( \text{PC9}_6^1 \) sequence was able to improve the polarization transfer by about 10\% using CW-decoupling. This result was later on confirmed numerically using the GAMMA\[37\] environment.

In Section 2.7, we have demonstrated that protons XiX-decoupling characterised by its amplitude \( \nu_{1I} \) and its modulation frequency \( \nu_{m,\text{XiX}} \) is a viable alternative to CW-decoupling when the TOBSY sequence \( \text{PC9}_6^1 \) is used on carbons. We first found experimentally the good decoupling condition, where the XiX-modulation frequency equals the MAS spinning frequency, \( \nu_{m,\text{XiX}} = \nu_r \). This special condition could lead to a 10\% enhanced polarization transfer compared to CW-decoupling at a relatively strong rf-field intensity (\( \nu_{1I} \geq 180 \text{ kHz} \)), while being quite inefficient at lower intensities. This results could also be fully confirmed numerically using GAMMA\[37\]. Afterwards, increasing the modulation frequency \( \nu_{m,\text{XiX}} \), we found that when the XiX-modulation frequency equals the rf-field intensity used on the S-spins channel (here \( ^{13}\text{C} \)), namely \( \nu_{m,\text{XiX}} = \nu_{1S} \), a noticeable increase in polarization transfer could be observed, especially at lower decoupling-field intensity (\( \nu_{1I} \leq 160 \text{ kHz} \)). A GAMMA\[37\] simulation was able to reproduce quantitatively this condition. A common point between both XiX-decoupling schemes with \( \nu_{m,\text{XiX}} = \nu_r \) as well as \( \nu_{m,\text{XiX}} = \nu_{1S} \) is the much smoother behaviour of the polarization transfer with respect to the decoupling field intensity compare to CW-decoupling which exhibits many more resonance conditions.

In Section 2.8, we noticed that the condition \( \nu_{m,\text{XiX}} = \nu_{1S} \) could be expressed in two different manners using a dual-channel symmetry-based notation \( \text{PC9}_6^1 \text{CN}_n^\nu \). First, by defining a C-element as the juxtaposition of two rectangular pulses L of arbitrary flip-angle, the second one being \( \pi \)-phase-shifted with respect to the first one, we got:

\[
\nu_{m,\text{XiX}} = \nu_{1S} \equiv \text{PC9}_6^1 \text{LiL18}_6^0
\]

Second, with a rectangular pulse L of arbitrary flip angle instead of a C-element (we call the sequence so formed, a L-sequence) , we obtained:

\[
\nu_{m,\text{XiX}} = \nu_{1S} \equiv \text{PC9}_6^1 \text{L36}_6^{18}
\]
To generalize those two conditions to other possible decoupling sequences, we analysed the dual-rotor synchronised symmetry-based sequences $C_{96}^1CN_{n}^{\nu \neq 0}$ (without z-rotations) using Levitt’s Mathematica package [36] and obtained the minimum number of 11 symmetry-allowed terms in the average Hamiltonian. We did the same for the sequences of the form $C_{96}^1CN_{n}^{\nu = 0}$ (with z-rotations) leading this time to the minimum number of 7 symmetry-allowed terms in the average Hamiltonian. Finally, we assessed numerically dual rotor-synchronized symmetry-based TOBSY sequences of the type $PC_{96}^1LIL_{n}^{\nu = 0}$ (Subsection 2.8.1), $PC_{96}^1LIL_{n}^{\nu \neq 0}$ (Subsection 2.8.2) and $PC_{96}^1LIL_{n}^{\nu \neq 0}$ (Subsection 2.8.3). For each sequence, we simulated the polarization transferred to spin $C_2$ from spin $C_1$ in a four spin system $C_2C_1H_1H_2$ as a function of the decoupling field intensity $\nu_{1I}$ and mixing time $t_{mix}$ and finally compared their efficiency at a constant mixing-time $t_{mix}$ as a function of $\nu_{1I}$.

The common trait of all the dual-channel symmetry-based sequences is the smoother behaviour with respect to the rf-amplitude of the decoupling of the transferred polarization compared to CW-decoupling. We found many sequences having a higher transfer for the $\nu_{1I} \leq 160$ kHz region, that one being of extreme importance for protein NMR to avoid sample degradation. We found especially the sequences $PC_{96}^1L18_8^8$ and $PC_{96}^1L36_6^{17}$ and their minus-$\nu$ counterparts $PC_{96}^1L18_6^8$ and $PC_{96}^1L36_6^{19}$ which appear very promising and should work best if decoupling field intensities $\nu_{1I} \geq 160$ kHz are available.

### 2.10. Outlook

It may be interesting to try other form of decoupling, for instance the dual-channel symmetry-based sequences derived in Section 2.8 with the supercycled version $PC_{96}^1$ of Section 2.6 to see if the improved polarization transfer could be maintained or reinforced. In order to verify the promising higher polarization transfer simulated with the sequences $PC_{96}^1L18_6^8$ and $PC_{96}^1L36_6^{17}$ and their minus-$\nu$ counterparts $PC_{96}^1L18_8^8$ and $PC_{96}^1L36_6^{19}$, those latter should be experimentally assessed on a spectrometer.

Overall, we can conclude that the heteronuclear decoupling under magic angle spinning is a fully coherent process involving I and S spins, and that the assumption that “the I-spins are perfectly decoupled” is not always experimentally met, especially with samples containing protons. One
should therefore be cautious, when developing homonuclear sequences without taking care of the heteronuclear couplings. This work has shown that the many resonance conditions present when using CW-decoupling could be efficiently reduced by using dual-channel symmetry-based rotor-synchronised decoupling sequences for which the polarization transfer obtained is much smoother with respect to the decoupling-field intensity.

To conclude, we believe that the future of heteronuclear decoupling for high-resolution solid-state NMR, lies fully in the region $\nu_{1I} \leq 160$ kHz relevant for protein NMR. Along this line, we may cite the recent high-phase TPPM heteronuclear decoupling scheme\cite{53}, whose efficiency in this decoupling-field intensity range is due to the quenching of the rotary resonance (RR) conditions $\nu_1 = n \nu_r$ with $n=1,2$. As shown in this work, there is room for improvement in trying other phase- and/or amplitude-modulated decoupling schemes at moderate MAS frequency. Especially in the context of C/R sequences, as the symmetry-based theory tells nothing about the form of the basic elements, we believe there is is room for improvement. For instance, we will propose in Chapter 3 a basic element formed by the concatenation of two dipole-compensated pulses, the second one being $\pi$-phase-shifted with respect to the first one. We will see that those pulses efficiently generate polarization echoes at a rate higher than magic-angle spinning, thus helping MAS in averaging out homonuclear dipolar interactions.
Figure 2.10.: Experimental transferred polarization (CH$_3$) using the sequence PC9 on the carbons. The sample used was 2,3-$^{13}$C-sodium propionate. The measurements were performed on a Varian Infinity+ 500 MHz spectrometer using a 1.8 mm MAS probe (Experiment done together with Ingo Scholz). Mixing time dependence of the polarization transfer for a constant decoupling field intensity $\nu_{1I}=225$ kHz in the case of a) CW-decoupling and c) XiX-decoupling with $\nu_{m,XiX}=\nu_r$. Decoupling field intensity dependence of the transferred polarization for the constant mixing time $t_{mix}=9$ ms for b) CW-decoupling and d) XiX-decoupling with $\nu_{m,XiX}=\nu_r$. 

transfer: CH$_2$ → CH$_3$
Decoupling during TOBSY Sequences

Figure 2.11.: a) Experimental and b) Simulated transfer $C_\alpha$→CO for Glycine-ethylester. The TOBSY sequence used was PC96, while XiX-decoupling was used for proton decoupling. The XiX-modulation frequency $\nu_{m,XiX}$ range was from 10 to 100 kHz, corresponding to a $\nu_{m,XiX}/\nu_r$ range from 0.4 to 4 ($\nu_r=25$ kHz) which is about four times the range of Figure 2.9. The decoupling rf-field intensity $\nu_{1I}$ from 0 to 200 kHz was also much larger than the one in Figure 2.9. The MAS frequency was set to $\nu_r=25$ kHz.
Figure 2.12: Simulated transfer $C_{\alpha} \rightarrow CO$ for Glycine-ethylester using the $PC(\chi)_{4}$ sequence with $\nu_r = 25 \text{kHz}$ and $\nu_{1S} = 75 \text{kHz}$. We used a four-spins system corresponding to Glycine-ethylester with the parameters given in Table 2.1(a). a) XiX-decoupling with $\nu_{m} = \nu_{r}$ b) XiX-decoupling with $\nu_{m,XiX} = 3\nu_{r} = \nu_{1S}$ c) CW-decoupling d) as in b) but with $J_{CC}$ set to 0
Figure 2.13: Simulated transfer $C_{\alpha}\rightarrow CO$ for Glycine-ethylester. The sequence used was PC91 with $\nu_r=25\text{kHz}$ and $\nu_{1S} = 75\text{kHz}$. Mixing-time dependence of the three different decoupling schemes as listed in the legend. For the curve in red, we set $J_{\text{CC}} = 0$, meaning that the transfer observed is dipolar in origin. For a CW-decoupling field intensity of $\nu_{1I} = 75\text{kHz}$ (vertical dashed line), we observe an enhanced transferred polarization. This is probably due to the absence of resonance conditions at this intensity. This frequency (75 kHz) is exactly the one corresponding to the XiX-modulation frequency $\nu_{m,XiX} = 3\nu_r = \nu_{1S}$ and is probably what explains the efficiency of the XiX-sequence with that modulation frequency.
Figure 2.14: Simulated polarization transfer \( <S_{2z}> \) in a four-spins system \( C^2 H^1 H^2 \) with the parameters given in Table 2.1a) using PC916\(CN^\nu\) also denoted \([N \ n \ \nu]\). a)\([18 \ 6 \ 0]\) b)\([36 \ 6 \ 0]\) c)\([45 \ 6 \ 0]\) d)\([54 \ 6 \ 0]\) e)CW-decoupling f)Slices at constant mixing time \( t_{\text{mix}} = 9.8 \text{ ms} \) out of a) to e) showing the polarization transfer \( <S_{2z}> \) as a function of the rf-decoupling intensity \( \nu_{1,1} \). Note that the sequence \([18 \ 6 \ 0]\) corresponds to the decoupling condition \( \nu_{m,X1X} = \nu_{1S} \).
Figure 2.15: Simulated polarization transfer $<S_{2z}>$ in a four-spins system $C^2 C^1 H^1 H^2$ with the parameters given in Table 2.1a) using PC916 CN also denoted $[N n ν]$. a)$[63 6 0]$ b)$[72 6 0]$ c)$[81 6 0]$ d)$[90 6 0]$ e)CW-decoupling f)Slices at constant mixing time $t_{mix} = 9.8$ ms out of a) to e) showing the polarization transfer $<S_{2z}>$ as a function of the rf-decoupling intensity $ν_{1,1}$.
Figure 2.16.: Simulated polarization transfer $<S_{2z}>$ in a four-spins system $C^2C^1HH$ with the parameters given in Table 2.1a) using PC916 also denoted $[N \nu]$ a)18 6 1] b)]18 6 9] c))[18 6 17] d)CW-decoupling e)Slices at constant mixing time $t_{mix}=9.8 \text{ ms}$ out of a) to d) showing the polarization transfer $<S_{2z}>$ as a function of the rf-decoupling intensity $\nu_1,I$. 

![Figure 2.16](image-url)
Figure 2.17: Simulated polarization transfer $<S_{2z}>$ in a four-spins system $C^2C^1H^1H^2$ with the parameters given in Table 2.1a) using PC916 also denoted $[N n \nu]$. a)$[27 6 9]$ b)$[27 6 18]$ c)$[36 6 18]$ d)$[36 6 27]$ e)CW-decoupling f)Slices at constant mixing time $t_{mix} = 9.8$ ms out of a) to e) showing the polarization transfer $<S_{2z}>$ as a function of the rf-decoupling intensity $\nu_{1,1}$. 
Figure 2.18: Simulated polarization transfer $<S_{2z}>$ in a four-spins system $^1H_1^1H_2$ with the parameters given in Table 2.1a) using $PCO_{60}^6CN_n'$ also denoted $[N_n \nu]$. a)$[54 6 18]$ b)$[54 6 27]$ c)$[54 6 36]$ d)CW-decoupling e)Slices at constant mixing time $t_{mix} = 9.8 \text{ ms out of a) to d) showing the polarization transfer } <S_{2z}>$ as a function of the rf-decoupling intensity $\nu_{1,1}$. 
Figure 2.19: Simulated polarization transfer $<S_{zz}>$ in a four-spins system $C^2 C^2 H^1 H^2$ with the parameters given in Table 2.1 using PC$9_1$ parameters for GlyEth $C2C1HH$ at $500$MHz, also denoted $[N \ n \ \nu]$. a)[63 6 18] b)[63 6 27] c)[63 6 36] d)[63 6 45] e)CW-decoupling f)Slices at constant mixing time $t_{mix} = 9.8$ ms out of a) to e) showing the polarization transfer $<S_{zz}>$ as a function of the rf-decoupling intensity $\nu_{1,1}$. 

[Diagram of simulated polarization transfer with various parameters and plots showing the change in polarization with time and decoupling intensity.]
Simulated polarization transfer $<S_{2z}>$ in a four-spins system $C^2 NH HP HP$ with the parameters given in Table 2.1a) using $PO_{916} LN_n$ also denoted $L[N, n, \nu]$. a) $L[1868]$, b) $L[1869]$, c) $L[18610]$, d) CW-decoupling e) Slices at constant mixing time $t_{mix} = 9.8 \text{ ms}$ out of a) to d) showing the polarization transfer $< S_{2z} >$ as a function of the rf-decoupling intensity $\nu_1,I$. 

**Figure 2.20.**
Figure 2.21.: Simulated polarization transfer $<S_{2z}>$ in a four-spins system $C^2C^2H^1H^2$ with the parameters given in Table 2.1(a) using $PO_{91}^6CN_{16}^n$ also denoted $L[N,n]$. a)$L[36 \ 6 \ 17]\ b)L[36 \ 6 \ 18]\ c)L[36 \ 6 \ 19]\ d)CW-decoupling\ e)Slices at constant mixing time $t_{mix} = 9.8\ ms\ out\ of\ a)$ to d) showing the polarization transfer $< S_{2z} >$ as a function of the rf-decoupling intensity $\nu_{1,I}$. Note that the sequence $PO_{91}^6L36_{18}^n$ corresponds to the decoupling condition $\nu_{m,XIX} = \nu_{18}$. 

\[ L[36 \ 6 \ 18] \equiv (\nu_{m,XIX} = \nu_{18}) \]
Figure 2.22: Simulated polarization transfer $<S_{2z}>$ in a four-spins system $C^2C^1HH$ with the parameters given in Table 2.1a) using $POCI_6CN^{\nu_n}$ also denoted $L[N\ n\ \nu]$. a) $L[72\ 6\ 36]$ b) $L[72\ 6\ 36]$ c) $L[72\ 6\ 35]$ d) CW-decoupling e) Slices at constant mixing time $t_{mix} = 9.8\ ms$ out of a) to d) showing the polarization transfer $<S_{2z}>$ as a function of the rf-decoupling intensity $\nu_1$.\n
3. Dipole-Compensated Adiabatic Pulses

3.1. Introduction

In this chapter we introduce adiabatic inversion pulses with the property of averaging out homonuclear dipolar couplings. In Section 3.2 we first recall the transformation properties of homonuclear dipolar interaction in a strong effective field tilted away from the +z-axis on the Bloch sphere by an angle $\theta$, namely that they scale like second-order Legendre polynomials $P_2(\cos(\theta))$ upon which both magic echo\cite{54} and polarization echo\cite{55} are based. The basic idea introduced in this work is to render the function $\theta$ time-dependant and to shape it such that the time-average of the scaling factor $P_2(\cos(\theta(t)))$ vanish over a time $t_{\text{inv}}$. We call the process of shaping the function $\theta(t)$ to average out specific interactions “theta-averaging”. We also choose the boundary conditions for the function $\theta(t)$ to be consistent with an inversion pulse of duration $t_{\text{inv}}$, i.e. $\theta(t = 0) = 0$ and $\theta(t_{\text{inv}}) = \pi$. Because of the xy-plane reflection symmetry of the second-order Legendre polynomials, an inversion pulse generates two polarization echoes, the first one when the effective field lies in the xy-plane and the second one when the effective field lies along the -z-axis. In the following, we call such adiabatic inversion pulses “dipole-compensated adiabatic pulses”. In Section 3.3 we define the adiabaticity factor $Q$ and describe four adiabatic inversion pulses, two standard pulses: $\text{sech}$ (Subsection 3.3.1) and $\text{WURST}$ (Subsection 3.3.2) and two dipole-compensated inversion pulses $\text{complin}$ (Subsection 3.3.3) and $\text{compsech}$ (Subsection 3.3.4). We prove in Subsection 3.3.6 that for on-resonance spin packets, the time-average of the scaling factor $P_2(\cos(\theta(t)))$ vanishes in the case of $\text{complin}$ and $\text{compsech}$ contrary to the standard adiabatic pulses $\text{sech}$ and $\text{WURST}$. In Section 3.4 we perform extensive GAMMA\cite{37} polarization transfer simulations on a two-spin $^{13}\text{C}^{13}\text{C}$ system and varying the dipolar strength $d_{\text{CC}}/2\pi$ and chemical shifts $\Omega$ which prove the viability of the concept of theta-averaging in generating polarization echoes. Finally, in Section 3.5 we use the concatenation of two $\text{complin}$ pulses, the second one $\pi$-phase-shifted with respect to the first one, as a C-element in the TOBSY sequence.
complin and compare the polarization transfer on a 2,3-\textsuperscript{13}C-sodium propionate with the sequence WiW\textsuperscript{9}\textsuperscript{124}, where the complin pulses are replaced by WURST pulses. The 10\% enhanced polarization transfer of the complincomplin\textsuperscript{9}\textsuperscript{124} over the WiW\textsuperscript{9}\textsuperscript{124} sequence observed experimentally could be later on fully confirmed numerically.

3.2. Theoretical Derivation

Considering a static solid containing a single nuclear spin species $S$, we can write a spin Hamiltonian of the form

$$\mathcal{H} = \mathcal{H}_S + \mathcal{H}_{SS} + \mathcal{H}_{rf},$$

where

$$\mathcal{H}_S = \sum_i \Omega_i^S S_i z,$$

with $\Omega_i^S$ the isotropic chemical shift of nucleus $i$, and

$$\mathcal{H}_{SS} = \sum_{i<j} \omega_{ij}^{SS} \cdot (3S_i z S_j z - S_i \cdot S_j).$$

Here $\omega_{ij}^{SS}$ are the orientation-dependent homonuclear dipolar couplings among the $S$ spins which are defined as\cite{56}:

$$\omega_{ij}^{SS} = -(\mu_0/4\pi)(\gamma_S^2 \hbar/r_{ij}^3)P_2(\cos(\theta_{ij}))$$

with $\theta_{ij}$ the angle of the internuclear vector $r_{ij}$ with respect to the main field $B_0$, $\gamma_S$ the gyromagnetic ratio of spin $S$ and the second-order Legendre polynomial $P_2(\cos \theta)$ defined as:

$$P_2(\cos \theta) = \frac{1}{2} (3 \cos^2(\theta) - 1)$$

In this chapter, we use a rf Hamiltonian of the form:

$$\mathcal{H}_{rf}(t) = \omega_{1S}(t)F_x + \Delta \omega_S(t)F_z$$

with $\omega_{1S}$ the rf-field amplitude, $\Delta \omega_S$ the carrier frequency offset from the Larmor frequency of the spin under study. The $F_\alpha$ denote the total spin operators (e.g. $F_x = \sum_i S_i z$). Scalar couplings and chemical-shift anisotropies are neglected. By transforming now the Hamiltonian into a tilted frame, we can have the effective field aligned along the new quantization axis $z'$.
Figure 3.1: Graphical representation of the effective field $\nu_{\text{eff}}$. $\nu_1$ is the rf-field intensity whereas $\Delta \nu$ is the frequency offset from the carrier frequency. The orientation of $\nu_{\text{eff}}$ is along the new quantization axis $z'$.

(see Figure 3.1). The tilted Hamiltonian is obtained by the unitary transformation:

$$ \mathcal{H}' = U_{\text{tilt}} \mathcal{H} U_{\text{tilt}}^\dagger $$ \hspace{1cm} (3.7)

with

$$ U_{\text{tilt}} = \exp [+i(\theta_S F_y)] \hspace{1cm} (3.8) $$

The effective field is characterized by its amplitude $\omega_{\text{eff}}$ and is inclined from the $+z$-axis by the angle $\theta_S$.

$$ \omega_{\text{eff}} = \sqrt{\frac{\omega_{1S}^2 + \Delta \omega_S^2}{\omega_{1S}^2}} \hspace{1cm} (3.9) $$

$$ \theta_S = \text{atan} \left( \frac{\Delta \omega_S}{\omega_{1S}} \right) + \pi/2 \hspace{1cm} (3.10) $$

The inverse tangent function being multivalued, it requires the definition of a branch cut in the complex plane which defines its range. In this work, we use the branch cut defined in Mathematica\cite{57} which leads, for real arguments $x$ in $\text{atan}(x)$, to the range $[-\pi/2, \pi/2]$. With
this definition, we need to add $\pi/2$ to obtain for $\theta$ the range $[0, \pi]$. What remains now is to remove the effective rf-field $H_{\text{rf}} = \omega_{\text{eff}} F_z$ from the tilted-frame Hamiltonian by transforming it into an interaction-frame:

$$\hat{H}(t) = \exp(+i\mathcal{H}_{\text{rf}} t) \hat{H}' \exp(-i\mathcal{H}_{\text{rf}} t)$$  (3.11)

In the strong field approximation ($\omega_{\text{eff}} \gg \omega_{ij}^{SS}$), and keeping only the secular terms, we get

$$\hat{H}_{\text{sec}} = P_2(\cos \theta_{S}) \mathcal{H}^{SS} + \cos \theta_{S} \sum_i \Omega_i^{(i)} S_i z$$  (3.12)

In the interaction-frame, we thus obtain a scaled secular homonuclear dipolar interaction $\hat{H}^{SS}$:

$$\hat{H}^{SS} = P_2(\cos \theta_{S}) \mathcal{H}^{SS}$$  (3.13)

The scaling factor, which appears as a result of the truncation of the homonuclear dipolar interaction with respect to a strong effective field applied at a tilt angle $\theta_S$, is in our case the second-order Legendre polynomial $P_2(\cos \theta_{S}) \equiv \frac{1}{2}(3\cos^2 \theta_{S} - 1)$. The form of this factor is a direct consequence of the transformation properties of the homonuclear dipolar interaction as an irreducible tensor of rank two. This factor equals zero at the magic angles $\theta_{S} = \theta_m = \text{atan}(\sqrt{2}) \approx 54.7^\circ$ and $\theta_S = \pi - \theta_m = \pi - \text{atan}(\sqrt{2}) \approx 125.3^\circ$ (see Figure 3.2). A CW-irradiation with an off-resonance offset $\Delta \nu_{\text{LG}}$ and rf-field intensity $\nu_{1,\text{LG}}$ such that $\theta_{S} = \text{atan} \left( \frac{\Delta \nu_{\text{LG}}}{\nu_{1,\text{LG}}} \right) = \theta_m$ underlies the Lee-Golburg homonuclear decoupling scheme[58]. The frequency-switched Lee-Goldburg scheme is also based on the same principle, but in this case the effective field lies along the magic angle $\theta_m$ for a time $t_{p,\text{FSLG}}$ before changing abruptly its direction along the other magic angle $\pi - \theta_m$ in conjunction with a $\pi$-phase shift[59].

On the other hand, we also have that for angles $\theta_S$ in the range $\theta_m \leq \theta_S \leq \pi - \theta_m$, the scaling factor $P_2(\cos(\theta))$ changes sign. In particular, for on resonance irradiation, with $\Delta \nu = 0$ and consequently $\theta_S = \pi/2$ we have $P_2(\cos(\theta_S)) = -\frac{1}{2}$. This leads to an effective change of sign of the homonuclear dipolar interaction and is the basis of all homonuclear dipolar echo schemes. For instance, the magic-echo scheme[54] in its simplest form comprises two discrete evolution periods. A first $(\pi/2)_y$ pulse brings the polarization along the x-axis. This is followed by the first evolution period of duration $t_1$ which consists in a spin-lock on-resonance during which the homonuclear dipolar interactions $\mathcal{H}^{SS}$ scale as $-1/2 \mathcal{H}^{SS}$. The second evolution period, this time
of duration $t_2 = t_1/2$, let the coherences evolve under the unscaled homonuclear dipolar interactions $\mathcal{H}_{\text{SS}}$, i.e. without any irradiation. After a time $t=1.5t_1$ a coherence echo is formed. Zhang, Meier and Ernst were the first to demonstrate the possibility of polarization-echo formation.[55]

The underlying principle is, as for the magic echo, based on the change of sign of the scaling factor $P_2(\cos(\theta_S))$ during two consecutive evolution periods. In this case however, quoting from [55]: “It should be noticed that the total polarization [...] remains constant, and a frequency-selective or spatially-selective measurement technique is required to observe polarization-echo effects.” Those authors chose the first alternative by generating a nonequilibrium polarization state between chemically-shifted resonances which could subsequently evolve under a dipolar Hamiltonian to finally be refocussed. More specifically, this nonequilibrium state on abundant I-spins (protons) was generated by perturbing a rare spin species S (carbons) and exploiting the heteronuclear dipolar interaction between I and S spins. Thus, contrary to the magic-echo which refocusses coherences in the transverse plane, a longitudinal-mixing evolution requiring a starting nonequilibrium polarization is, in this case, needed to observe a polarization echo. The common condition for both magic and polarization-echo formation, using two discrete evolution periods $t_1$ and $t_2$ with the effective field tilted away from the +z-axis by angles $\theta_{1,S}$ and $\theta_{2,S}$ respectively, can be written as:

$$t_1 P_2(\cos \theta_{S,1}) + t_2 P_2(\cos \theta_{S,2}) = 0$$

The subject of this work is to generalize Equation 3.14 to the case where the angles $\theta_S$ can be described by a continuous time-dependent function $\theta_S(t)$. Besides, we choose the function $\theta_S(t)$ to be consistent with an adiabatic inversion of inversion time $t_{\text{inv}}$, i.e. with the boundary conditions $\theta_S(t_0) = 0$ and $\theta_S(t_{\text{inv}}) = \pi$. The final goal of this work will be to develop a dipole-compensated adiabatic inversion pulse able to refocus homonuclear dipolar evolution by making use of polarization echoes in the effective field. We argue now that Equation 3.14 can be generalized to the continuous form:

$$\int_0^{t_{\text{inv}}} P_2(\cos \theta_S(t))dt = 0$$

with $P_2(\cos \theta)$ the second-order Legendre polynomial, as defined in Equation 3.5 and depicted in Figure 3.2 and $t_{\text{inv}}$ the inversion time of the adiabatic pulse. Due to the xy-transverse plane of symmetry of second-order Legendre polynomials, we also have:

$$\int_0^{t_{\text{inv}}/2} P_2(\cos \theta_S(t))dt = 0$$
This basically means that we expect two polarization echoes during one inversion. The first echo should form on-resonance, when the effective field lies along the xy-transverse plane, while the second should form in the end of the inversion, far above resonance, when the effective field lies along the -$z$-axis on the Bloch sphere. We look for a function $\theta(t)$ such that the negative area exactly compensates the positive area. For this purpose, we need the effective field vector to spend more time in the region where the second-order Legendre polynomial is negative ($\theta_m \leq \theta \leq \pi - \theta_m$) with $\theta_m = \arctan(\sqrt{2})$ the magic angle, and consequently less time in the region where the scaling factor is positive. From now on, we call the concept of shaping the function $\theta(t)$ specifically so as to average out a given interaction depending on $\theta(t)$ over a time $t_{\text{inv}}$ theta-averaging.
3.3. Adiabatic Pulses

Adiabatic inversion pulses offer significant advantages over hard $\pi$ or composite $\pi$ radiofrequency pulses when the effective bandwidth is the important criterion. Furthermore, as their performance is almost independent of the radiofrequency level above a certain minimum, they are quite tolerant to radiofrequency inhomogeneities and miscalibrations. Contrary to the hard pulse version of inversion where the carrier frequency is kept on resonance, adiabatic inversion pulses are characterized by the sweeping of the carrier frequency from far below to far above resonance (or vice versa). As already pointed out in Section 3.2 in a frame rotating synchronously with the applied rf-field, we can define an effective field $\omega_{\text{eff}}$, which results from the rf-field $\omega_1$ and the resonance offset $\Delta \omega$ and is inclined by an angle $\theta = \tan(\Delta \omega/\omega_1) + \pi/2$ from the $+z$-axis.

To obtain an adiabatic inversion the angle $\theta$ should run from 0 (along the $+z$-axis, i.e. along the main field $B_0$) to $\pi/2$ (i.e. on-resonance) reaching finally $\pi$ (along the $-z$-axis, i.e. antiparallel to $B_0$). Note that a sweep for which $\theta = 0 \to \pi$ is equally possible. In order to maintain the magnetization vector along the effective field, the variation of $\theta$ should be much smaller than the rate at which the spins precess about the effective field, i.e.:

$$|d\theta/dt| \ll \omega_{\text{eff}} \quad (3.17)$$

Indeed, the adiabatic theorem\[9\] tells us that when this condition is met, the angle $\alpha$ (in our case $\alpha = 0$) of the polarization with the instantaneous direction of the field is a constant of motion. In order to quantify to which extent Equation 3.17 is fulfilled, it is customary to use the adiabaticity factor $Q$ which is defined as the ratio of the effective field intensity $\omega_{\text{eff}}(t)$ over the angular sweeping rate $\dot{\theta}(t)$:

$$Q(t) = \frac{\omega_{\text{eff}}(t)}{\dot{\theta}(t)} \quad (3.18)$$

where the dot refers to time-derivative.

The adiabaticity $Q$ can vary during the inversion. Because for a constant $\omega_{1S}$ the effective field is minimum on resonance, a pulse is often characterized by its $Q_0$ or $Q$ on resonance. Baum, Tycko and Pines showed numerically that a $Q_0$ of 5 leads to a good inversion \[60\]. Later, Kupče and Freeman demonstrated that a $Q$ larger than 5 is far too conservative and they obtained good inversions with $Q_0$ of about 1\[61\]. Recently, it has been argued that the $Q$ defined in Equation 3.18 does not described accurately the spin dynamics due to finite pulse duration.
effects, thus explaining why some low-Q pulses perform so well. To get a better approximation of the real Q, one should resort to an iterative transformation of the effective Hamiltonian describing the process into superadiabatic frames until the desired convergence is obtained[62].

In this work, we will consider a good inversion pulse as having a Q larger than 5 throughout the sweep.

### 3.3.1. Hyperbolic Secant Pulses: *sech*

The hyperbolic secant pulse or sech/tanh pulse, as introduced by McCall and Hahn [63], is a well-established adiabatic inversion pulse. The amplitude profile $\omega_1(t)$ of an hyperbolic secant pulse reads:

$$\omega_1(t) = \omega_{1,max} \text{sech} \left[ 2\gamma \left( \frac{t}{t_{\text{inv}}} - \frac{1}{2} \right) \right]$$

(3.19)

whereas its offset profile $\Delta \omega(t)$ with respect to the carrier frequency is given by:

$$\Delta \omega(t) = \frac{SW \tanh \left[ 2\gamma \left( \frac{t}{t_{\text{inv}}} - \frac{1}{2} \right) \right]}{2\tanh \gamma}$$

(3.20)

As usual, we use a constant carrier frequency channel, meaning this frequency modulation is implemented as a phase modulation $\phi(t) = \int_0^t \Delta \omega(\tau)d\tau$:

$$\phi(t) = SW \frac{t_{\text{inv}} \tanh \gamma}{4\gamma} \left\{ \ln \left( \cosh \left[ 2\gamma \left( \frac{t}{t_{\text{inv}}} - \frac{1}{2} \right) \right] \right) - \ln (\cosh [-\gamma]) \right\}$$

(3.21)

with $SW$ the sweepwidth, $\omega_{1,max}$ the maximum rf-field intensity and $\gamma$ a truncation-parameter. It is known that five is a good choice for $\gamma$ as it truncates at 1.3% of the maximum amplitude $\nu_{1,max}$[64] and this value will be used throughout this work.

Figure 3.3 shows the amplitude, offset and integrated offset profiles for an inversion pulse with $\nu_{1,max} = \omega_{1,max}/2\pi=100$ kHz and $SW=200$ kHz. From the amplitude $\nu_1(t)$ and the off-resonance offset $\Delta \nu(t)$ it is an easy task to compute the function $\theta(t)$ using Equation 3.10. This function is plotted on Figure 3.4a), while on Figure 3.4b) the second-order Legendre polynomial $P_2(\cos \theta(t))$ is depicted as a function of time. It is qualitatively evident that the small negative area cannot compensate the positive one, meaning Equation 3.15 is not fulfilled, and no polarization echoes are expected, neither after $t = t_{\text{inv}}/2$ nor $t = t_{\text{inv}}$. This pulse will serve as a reference in checking
the ability of the dipole-compensated pulses comlin and compsech of averaging out homonuclear dipolar couplings (see Subsection 3.3.3 and Subsection 3.3.4).

3.3.2. WURST Pulses

WURST pulses were introduced by Kupče and Freeman [61], WURST standing for wideband, uniform rate, smooth truncation. They pointed out that the problems of many adiabatic inversion pulses have been posed in an oversimplified manner, i.e. considering the inversion of a single spin species whereas in practice, it is the inversion over a wide range of chemical shift which matters. They argued that the key parameters - sweep rate, radiofrequency level, and adiabaticity - should be roughly constant throughout the frequency range of interest. They also pointed out that the hyperbolic secant, although providing an excellent inversion profile, is limited by its high peak radiofrequency amplitude which could damage the probe as well as the sample, as well as an inefficient distribution of radiofrequency power (see Figure 3.3). According to these authors the process of spin inversion could be broken down into three stages: a) Adiabatic departure from the +z axis. b) A central region where the sweep rate is constant. c) Adiabatic return to the -z axis. They proposed a constant-amplitude linear sweep for stage b) over the frequency range of interest, making sure that all spins within that range follow the same trajectories irrespective of offset. With this approach the function for the offset takes the linear form:

$$\Delta \omega(t) = SW/2(t - t_{\text{inv}}/2)$$

(3.22)

with SW the sweeping range and t_{inv} the inversion time (see Figure 3.6(b)), whereas the amplitude takes the "sausage" form (see Figure 3.6(a)):

$$\nu_1(t) = \nu_{1,\text{max}} (1 - |\sin(\beta t)|^n)$$

(3.23)

with $-\pi/2 \leq \beta t \leq \pi/2$, which is basically a boxcar function whose edges have been smoothed. The smoothing is determined by the parameter n; the larger the value of n, the sharper the cutoff at the edges and the more the amplitude shape looks like a boxcar function. In this work we used n=8. We used the same criterion as Hardy et al. (52) to determine the sweeping range necessary for a given adiabaticity factor $Q_0$. $Q_0$ is the adiabaticity factor in the center of the sweep where the amplitude equals $\nu_{1,\text{max}}$. With this criterion, we have a linear frequency sweep
3.3 Adiabatic Pulses

Figure 3.3.: a) amplitude $\nu_1(t)$, b) offset $\Delta \omega(t)/2\pi = \Delta \nu(t)$ and c) phase $\phi(t) = \int_0^t \Delta \omega(\tau) d\tau$ for use with constant carrier frequency for an hyperbolic secant pulse with $t_{inv}=60 \mu s$, $\nu_{1,max}=100 \text{kHz}$ and $SW=200 \text{kHz}$ with the three functions defined in Subsection 3.3.1.
Figure 3.4: Plot of a) $\theta(t)$ and b) $P_2(\cos \theta(t))$ as defined in Equation 3.5 for an hyperbolic secant pulse with $t_{\text{inv}}=60 \mu s$, $\nu_{1,\text{max}}=100 \text{kHz}$ and $SW=200 \text{kHz}$. To compute $\theta(t)$ from the rf-field amplitude $\nu_1(t)$ and off-resonance offset $\Delta \nu(t)$, we used Equation 3.10 with Equation 3.19 and Equation 3.20.
3.3 Adiabatic Pulses

with a constant frequency sweep rate of

\[ \Delta \omega(t) = \ddot{\phi}(t) = \omega_{1,\text{max}}^2 / Q_0 \]  

(3.24)

which can be integrated to give

\[ SW = 2\pi \nu_{1,\text{max}}^2 t_{\text{inv}} / Q_0 \]  

(3.25)

To get a \( Q_0 \) of five, for a maximum rf-amplitude \( \nu_{1,\text{max}} \) of 100 kHz, we get a sweepwidth of 754 kHz. In Figure 3.5 we show two GAMMA simulations showing the inversion of the total polarization of a two-spins system \(^{13}\text{C}^{13}\text{C}\) without couplings nor chemical shifts. We show the sum polarization evolution \( F_z \) after a WURST inversion pulses followed by a second WURST pulse, \( \pi \)-phase-shifted with respect to the first one, each having an inversion time of \( t_{\text{inv}} = 60 \mu s \).

We tried the two different sweepwidth of 200 kHz and 754 kHz. As can be seen, the inversion with \( SW = 200 \) kHz fails to invert completely the sum polarization even without couplings nor chemical shifts. As a consequence, we will used a sweepwidth \( SW = 754 \) kHz, a maximum rf-amplitude \( \nu_{1,\text{max}} = 100 \) kHz and an inversion time \( t_{\text{inv}} = 60 \mu s \) for all the WURST pulses of Chapter 3.

Figure 3.6a), b) and c) depict the amplitude, offset and phase profiles respectively using those parameters.

Using Equation 3.10 we can derive the angle \( \theta(t) \) from the amplitude \( \nu_1(t) \) and the offset \( \Delta \nu(t) \). Both functions \( \theta(t) \) and \( P_2(\cos(\theta(t))) \) are plotted in Figure 3.7a) and Figure 3.7b) respectively. We note that the negative area cannot compensate the positive one (i.e. Equation 3.15 is not fulfilled), and hence a polarization echo cannot be formed, neither after \( t = t_{\text{inv}}/2 \), nor after \( t = t_{\text{inv}} \). Thus, this pulse will serve as a second reference, along with the sech pulse described in Subsection 3.3.1, to check the efficiency of the dipole-compensated pulses \( \text{complin} \) (derived in Subsection 3.3.3) and \( \text{compsech} \) (derived in Subsection 3.3.4) in averaging out homonuclear dipolar couplings.

3.3.3. Compensated Pulse With Piecewise-linear Function \( \theta(t) \): \( \text{complin} \)

The simplest possibility to fulfill Equation 3.15 is to choose a linear function whose slope is flatter in the region between the two angles \( \theta_m \) and \( \pi - \theta_m \) which is defined as \( \text{domain 2} \) in Equation 3.31. This domain is also depicted graphically in Figure 3.8. If we define MF as the ratio of the positive over the negative area of the function \( P_2(\cos(\theta)) \) with \( \theta = 0 \to \pi \):
Figure 3.5: GAMMA[37] simulations showing the inversion profile of the sum polarization $F_z$ for a two-spins system $^{13}\text{C-}^{13}\text{C}$ without couplings nor chemical shifts. The inversion time is $t_{\text{inv}}=60\mu s$ and the maximum rf-amplitude is $\nu_{1,\text{max}}=100\text{kHz}$. The blue and red curves correspond to sweeping ranges $SW$ of $200\text{kHz}$ and $754\text{kHz}$ respectively. We computed two WURST-8 inversions, the second one being $\pi$-phase-shifted with respect to the first one. As seen on the figure, the WURST pulse with a sweeping range $SW$ of $200\text{kHz}$ fails to invert properly the sum polarization even without couplings nor chemical shifts. Throughout Chapter 3, we will therefore use WURST pulses with $SW=754\text{kHz}$ along with $\nu_{1,\text{max}}=100\text{kHz}$ and $t_{\text{inv}}=60\mu s$. 
3.3 Adiabatic Pulses

Figure 3.6.: a) amplitude $\nu_1(t)$, b) offset $\Delta \omega(t)/2\pi = \Delta \nu(t)$ and c) phase $\phi(t) = \int_0^t \Delta \omega(\tau) d\tau$ for use with constant carrier frequency for a WURST pulse with $t_{\text{inv}}=60\mu s$, $\nu_{1,\text{max}}=100\ kHz$ and $SW=754\ kHz$ with the three functions defined in Subsection 3.3.2.
Figure 3.7: Plot of a) $\theta(t)$ and b) $P_2(\cos \theta(t))$ as defined in Equation 3.5 for a WURST pulse with $t_{\text{inv}}=60 \mu$s, $\nu_{1,\text{max}}=100$ kHz and $SW=754$ kHz. To compute $\theta(t)$ from the rf-field amplitude $\nu_1(t)$ and off-resonance offset $\Delta \nu(t)$, we used Equation 3.10 with Equation 3.23 and Equation 3.24.
Figure 3.8.: Geometrical interpretation of the factor MF, as defined in Equation 3.26. The two domains defined by Equation 3.30 and Equation 3.31 are also depicted on the figure.

\[
MF = \frac{\int_{0}^{\theta_m} P_2(\cos \theta) d\theta}{\int_{\theta_m}^{\pi/2} P_2(\cos \theta) d\theta} = 2.96661
\]  
\[\text{(3.26)}\]

with \(\theta_m = \arctan \sqrt{2}\) the magic angle, and we choose the angular sweep-rate such that

\[
\dot{\theta}_1 = MF \dot{\theta}_2, \quad \text{(3.27)}
\]

we have stretched the time the effective field spends between the angles \(\theta_m\) and \(\pi - \theta_m\) by such an amount that Equation 3.16 and consequently Equation 3.15 are indeed fulfilled. Figure 3.8 gives a geometrical interpretation of the factor MF. Now we compute the two times \(t_1\) and \(t_2\) at which the effective field vector \(\nu_{\text{eff}}\) is inclined from the +z-axis at the angles \(\theta_m\) and \(\pi - \theta_m\) respectively (see Figure 3.2 and Figure 3.9):

\[
\begin{align*}
t_1 &= \frac{t_{\text{inv}}}{2} \left[ MF \left( \frac{\pi}{2\theta_m} - 1 \right) + 1 \right]^{-1} \quad \text{(3.28)} \\
t_2 &= t_{\text{inv}} - t_1 \quad \text{(3.29)}
\end{align*}
\]

We define now two angular domains as:

\[
\text{domain 1:} \quad 0 \leq \theta \leq \theta_m \quad \cup \quad \pi - \theta_m \leq \theta \leq \pi
\]  
\[\text{(3.30)}\]

\[
\text{domain 2:} \quad \theta_m \leq \theta \leq \pi - \theta_m
\]  
\[\text{(3.31)}\]

over which we get the desired angular sweeping rate \(\dot{\theta}_1\) and \(\dot{\theta}_2\) fulfilling Equation 3.27.
\[
\dot{\theta}(t) = \begin{cases} 
\dot{\theta}_1 & \text{if } t \leq t_1 \text{ or } t_2 \leq t \leq t_{\text{inv}} \\
\dot{\theta}_2 & \text{if } t_1 \leq t \leq t_2 
\end{cases} 
\] (3.32)

with
\[
\dot{\theta}_2 = \frac{(\pi/2 - \theta_m)/(t_{\text{inv}}/2 - t_1)}{\nu_1 \text{ max}} 
\] (3.33)
\[
\dot{\theta}_1 = \frac{\theta_m}{t_1} 
\] (3.34)

The angle \( \theta(t) \) is obtained as
\[
\theta(t) = \int_0^t \dot{\theta}(\tau) \, d\tau 
\] (3.35)

Figure 3.9a) shows the piecewise-linear function \( \theta(t) \) along with the second-order Legendre polynomial \( P_2(\cos \theta(t)) \) (Figure 3.9b)). It is seen that the negative area between the angles \( \theta_m \) and \( \pi - \theta_m \) (see Figure 3.2) exactly compensates the remaining positive areas near the poles. Note that this is true only on resonance. If chemical shifts are introduced, their effect will be to modify the function \( \theta(t) \) such that Equation 3.15 no longer applies hence hindering the polarization-echoes formation. This point will be discussed more extensively in Subsection 3.3.6.

After having chosen a suitable function \( \theta(t) \), we need to select a function for the effective field intensity \( \nu_{\text{eff}}(t) \). To be consistent with the shape of the function \( \theta(t) \) which we have already fixed, the effective field intensity must be of the form \( \nu_{\text{eff}}(\theta(t)) \). We choose here an elliptical function and as semi-axis the half of the sweepwidth \( SW/2 \) and the maximal rf-field intensity \( \nu_{1, \text{max}} \):
\[
\nu_{\text{eff}}(\theta(t)) = \left[ \left( \frac{\cos \theta(t)}{SW/2} \right)^2 + \left( \frac{\sin \theta(t)}{\nu_{1, \text{max}}} \right)^2 \right]^{-1/2} 
\] (3.36)

What remains is now to project the effective field on the z-axis to obtain the offset, and on the x-axis to get the amplitude as a function of time:
\[
\nu_1(t) = \nu_{\text{eff}}(\theta(t)) \cos \theta(t) 
\] (3.37)
\[
\Delta \nu(t) = \nu_{\text{eff}}(\theta(t)) \sin \theta(t) 
\] (3.38)

Note that this process of deriving the amplitude and offset from the function \( \theta(t) \) and effective field \( \nu_{\text{eff}}(t) \) is exactly the opposite of standard approaches where the offset and amplitude
functions are first chosen and the effective field $\nu_{\text{eff}}$ and adiabaticity factor $Q(t)$ then computed therefrom as was done in Subsection 3.3.1 and Subsection 3.3.2 for sech and WURST pulses respectively.

### 3.3.4. Compensated Pulse With a Smoother Function $\theta(t)$: $\text{compsech}$

From an adiabatic point of view, it is evident that the piecewise-linear version of the compensated pulse is not optimal. First the two kinks seen in the function $\theta(t)$ in Figure 3.9 should be avoided as they could generate transients. Second, to maximise the adiabaticity factor during the inversion, from Equation 3.18 it is evident that the angular sweeping rate should be as small as possible, or in other words, the slope of the function $\theta(t)$ should be as flat as possible. This is especially true near the poles on the Bloch sphere, where the rf-power is lowest [65]. Moreover, this condition of zero-slope for $\theta(t)$ at the beginning and the end of the sweep is indeed met in the case of both standard inversion pulses sech (see Figure 3.4a)) and WURST (Figure 3.7a)) which are known to provide very high inversion efficiency. However, for a fixed inversion time $t_{\text{inv}}$, due to the boundary conditions on $\theta$, i.e. $\theta(t=0)=0$ and $\theta(t_{\text{inv}})=\pi$, a region where the curve $\theta(t)$ is flat will unfortunately lead to a region where the curve is steep, meaning a low adiabaticity factor $Q$ over that region. Practically, because the rf-field intensity is not unlimited, the highest value of the slope $\dot{\theta}(t)$ will be given by the minimum quality factor $Q_{\text{min}}$ we can tolerate (see the definition of $Q(t)$ in Equation 3.18).

We propose here a second version of compensated pulses with a much smoother version of $\theta(t)$ and with a zero slope at the beginning and at the end of the sweep, meaning a very high $Q$ factor near the poles. As in Subsection 3.3.3 we first choose the desired function $\theta(t)$. This latter is given by:

$$
\theta(t) = \begin{cases} 
\frac{\pi}{4} \tanh \left[ 6 \sinh \left( \frac{t}{t_{\text{inv}}/2} - 2 \right) \right] + \frac{\pi}{4} & \text{if } t/t_{\text{inv}} \leq 1/2 \\
-\frac{\pi}{4} \tanh \left[ 6 \sinh \left( \frac{t_{\text{inv}} - t}{t_{\text{inv}}/2} - 2 \right) \right] + \frac{3\pi}{4} & \text{if } t/t_{\text{inv}} > 1/2 
\end{cases} 
$$

(3.39)

Figure 3.11 again confirms that the average of the secular homonuclear dipolar Hamiltonian is zero over one inversion (condition Equation 3.15) for on-resonance spin packets. For the effective field intensity, we again choose the elliptical form Equation 3.36 along with $\nu_{1,\text{max}}=100\text{kHz}$ and
Figure 3.9: Plot of a) $\theta(t)$ from Equation 3.35 and b) $P_2(\cos \theta(t))$ as defined in Equation 3.5 for an inversion time $t_{inv}=60 \mu s$. The times $t_1$ and $t_2$ defined by Equation 3.29 and Equation 3.28 amount, for an inversion time $t_{inv}=60 \mu s$, to 10.3 and 49.7 $\mu s$ respectively. For comparison, the dashed line also show the function $P_2(\cos(\theta(t))$ for a linear function $\theta(t)$ from which the stretching of the negative area of the function $P_2(\cos(\theta(t)))$ in the case of the complin pulse is evident.
3.3 Adiabatic Pulses

**Figure 3.10.**: a) amplitude $\nu_1(t)$, b) offset $\Delta \omega(t)/2\pi = \Delta \nu(t)$ and c) phase $\phi(t) = \int_0^t \Delta \omega(\tau) d\tau$ for use with constant carrier frequency for a complin compensated pulse with $t_{\text{inv}}=60 \mu s$, $\nu_{1,\text{max}}=100 \text{ kHz}$ and $SW=200 \text{ kHz}$.
SW = 200 kHz. Note that this function is not unique and other functions with better properties are certainly possible.

### 3.3.5. Adiabaticity Factors \( Q(t) \)

We calculate now the adiabaticity factors \( Q(t) \) as defined in Equation 3.18 for the four different adiabatic pulses considered. For the three inversion pulses \( \text{sech} \), \( \text{complin} \) and \( \text{compsech} \) we used a maximum rf-field intensity \( \nu_{1,\text{max}} = 100 \) kHz, a sweepwidth \( \text{SW} = 200 \) kHz and an inversion time \( t_{\text{inv}} = 60 \) µs. A GAMMA\textsuperscript{37} simulation with a two-spin \(^{13}\text{C},^{13}\text{C}\) system without couplings nor chemical shifts showed that a WURST pulse with such parameters lead to an incomplete inversion (see Figure 3.5). Therefore, keeping the same inversion time and maximal rf-field intensity, we extended the sweeping range to 754 kHz and thus obtained a \( Q_0 = 5 \) in the middle of the sweep (as in [52]) and a full inversion. A GAMMA\textsuperscript{37} simulation with the same parameters also proved that the three inversion pulses \( \text{sech} \), \( \text{complin} \) and \( \text{compsech} \) could lead to a full inversion for \( \text{SW} = 200 \) kHz, \( \nu_{1,\text{max}} = 100 \) kHz and \( t_{\text{inv}} = 60 \) µs (see Figure 3.16). The minimum adiabaticity factors of the four considered adiabatic pulses has been chosen higher than four, which is our criterion for good adiabatic inversion (see Section 3.3). The adiabaticity factors \( Q(t) \) for the four inversion pulses are depicted in Figure 3.13a) to Figure 3.13d). The vertical scale has been cut to 100.

Figure 3.13a) shows the adiabaticity factor \( Q(t) \) as a function of time for the hyperbolic secant pulse. We find the critical region located in the middle of the sweep, where the rf-intensity is maximal. This is consistent with the slope of the function \( \theta(t) \) which, for \( \text{sech} \), is maximal on resonance (see Figure 3.4a)). For the parameters used, the minimum adiabaticity factor \( Q_{\text{min}} \) reaches about 4. Far off-resonance, i.e. at the beginning and at the end of the sweep (here \( \Delta \nu = \pm 100 \) kHz), the adiabaticity factor \( Q \) becomes very large. This is explained by Equation 3.18 with, in the denominator, the angular sweep rate \( \dot{\theta}(t) \). As is seen from the top of Figure 3.4 the slope of \( \theta(t) \) with respect to time, which is also the angular sweeping rate, reaches zero far off-resonance.

In Figure 3.13b) we plot the function \( Q(t) \) as a function of time for the WURST pulse. In this case, the function \( Q(t) \) is very similar to the one for the \( \text{sech} \) pulse (Figure 3.13a)) with
Figure 3.11: Plot of a) $\theta(t)$ using Equation 3.39 and b) $P_2(\cos \theta(t))$ as defined in Equation 3.5 for an inversion time $t_{inv}=60 \mu s$. 
Figure 3.12.: a) amplitude $\nu_1(t)$, b) offset $\Delta \omega(t)/2\pi = \Delta \nu(t)$ and c) phase $\phi(t) = \int_0^t \Delta \omega(\tau) d\tau$ for use with constant carrier frequency for a compsech compensated pulse with $t_{\text{inv}}=60 \mu s$, $\nu_{1,\text{max}}=100 \text{ kHz}$ and $SW=200 \text{ kHz}$. 
the critical region with lowest adiabaticity factor in the center of the sweep. The minimum adiabaticity factor $Q_{\text{min}}$ amounts to 5, as in this case we selected the sweeping range $SW$ using Equation 3.25 to obtain this specific value. Far below the resonance frequency, at $-SW/2$ and far above it, at $+SW/2$ we again find a flat slope for the function $\theta(t)$ (see Figure 3.7a)) leading to a zero angular sweeping rate $\dot{\theta}(t)$ and consequently an infinite adiabaticity factor.

Figure 3.13c) depicts the same adiabaticity factor for complin as derived in Subsection 3.3.3. At first sight, we do not observe any infinite asymptotic regions over the sweep. This can again be explained by Equation 3.18 where in this case $\dot{\theta}(t)$ has been restricted to two values only $\dot{\theta}_1$ and $\dot{\theta}_2$ in order to fulfill Equation 3.15. This results in having the minimum adiabaticity of 6.8 at the boundaries of the sweeping range $-SW/2$ and $+SW/2$. Besides, the conditions chosen here, i.e. $\nu_{1,\text{max}} = 100$ kHz and $SW = 200$ kHz with the elliptical effective field intensity Equation 3.36 result in a constant effective field $\nu_{\text{eff}} = 100$ kHz throughout the sweep. From the definition of $Q$, we thus obtain two regions of constant adiabaticity delimited by the by $t_1 = 10.3 \mu s$ and $t_2 = 49.7 \mu s$ as in Figure 3.9 with, in this special case, $Q_{\text{max}} = MF Q_{\text{min}}$. We can also note a discontinuity of the function $Q(t)$ at the times $t_1$ and $t_2$ as defined in Equation 3.28 and Equation 3.29, where the function $\theta(t)$ equals the magic angles $\theta_m$ and $\pi - \theta_m$ respectively (see Figure 3.2).

In Figure 3.13d), we plot the same function $Q(t)$, this time for compsech (see Subsection 3.3.4). The first idea behind compsech was to set to zero the slope of the function $\theta(t)$ at the boundaries of the sweep $-SW/2$ and $+SW/2$, or for a broad-enough sweepwidth, near the poles $\pm z$ on the Bloch sphere. The desired function $\theta(t)$ had to be much smoother than the one of complin and avoid discontinuities. As a final condition, the function $\theta(t)$ should fulfill Equation 3.15 or the numerical integral should be as close to zero as possible. A function meeting those three requirements was given in Subsection 3.3.4. From the figure, we see indeed that the adiabaticity $Q(t)$ reaches infinity at the beginning and the end of the pulse. Another good point is the very large adiabaticity factor on resonance. This time however the critical points are not on-resonance but at the two regions where the slope $\dot{\theta}(t)$ is maximal on Figure 3.11 ($t \approx 10$ and $50 \mu s$) and the minimum adiabaticity factor amounts here to 4.1.

Note that constant adiabaticity dipole-compensated inversion pulses are possible as well. To
construct such pulses, one first has to choose a suitable function $\theta(t)$ fulfilling Equation 3.15. The effective field intensity $\nu_{\text{eff}}(t)$ is then derived by fixing $Q(t)$ to a constant value in Equation 3.18. Finally, the amplitude $\nu_1(t)$ and offset $\Delta\nu(t)$ can be derived by projecting the effective field on the x- and z-axis respectively (see Equation 3.37 and Equation 3.38).

### 3.3.6. Averaging out Homonuclear Dipolar Couplings

In order to check Equation 3.15 and the bandwidth over which it is valid, we replace the function $\theta(t)$ from Equation 3.10 by the more general form $\theta_{\text{CS}}(t, \Omega)$ which takes the chemical shift $\Omega$ directly into account:

$$\theta_{\text{CS}}(t, \Omega) = \text{atan} \left( \frac{\Delta\nu(t) - \Omega}{\nu_1(t)} \right) + \pi/2$$  \hfill (3.40)

with $\Delta\nu(t)$ the offset from the carrier-frequency, $\nu_1(t)$ the rf-field intensity and $\Omega$ the chemical shift. Indeed, Equation 3.15 has been derived for on-resonant spin packets, i.e. for $\Omega = 0$ Hz, and for off-resonant spins, we will get a chemical-shift-dependant angle $\theta$ given by Equation 3.40.

To assess the magnitude of the residual homonuclear dipolar coupling, we compute

$$Y(\Omega) = \log_{10} \left( \int_{t=0}^{t_{\text{inv}}} P_2(\cos \theta_{\text{CS}}(t, \Omega)) \, dt \right)$$ \hfill (3.41)

Figure 3.14 depicts the function $Y(\Omega)$ for the four adiabatic pulses discussed in this work with the chemical-shift range [-7 kHz,7 kHz]. As expected, neither the hyperbolic secant pulse $\text{sech}$ nor the $\text{WURST}$ pulse show any dip at the position $\Omega=0$, meaning this kind of adiabatic pulses is in principle unable to lead to the formation of polarization echoes. The value of the function $Y(\Omega)$, which is almost constant over the chosen chemical shift range, is nearly equal for both pulses and amounts to about -4.5 and -4.3 for $\text{WURST}$ and $\text{sech}$ respectively.

On the other hand, a marked dip is seen on resonance (i.e. without chemical shifts) for both dipole-compensated pulses $\text{complin}$ and $\text{compsech}$. The dip of $Y(\Omega)$ reaches about -13 and -12 for $\text{complin}$ and $\text{compsech}$ respectively. This is about 8-9 orders of magnitude less compared to the standard pulses $\text{sech}$ and $\text{WURST}$. Besides, the function $Y(\Omega)$ stays below -7 for both dipole-compensated pulses over the chemical-shift range [-7 kHz,7 kHz]. The higher value of $Y(\Omega)$ in the case of $\text{compsech}$ compared to $\text{complin}$ should in principle be compensated by their better adiabatic behaviour.
3.3 Adiabatic Pulses

Figure 3.13.: adiabaticity factors $Q(t)$ of the four considered adiabatic pulses: a) hyperbolic secant sech b) WURST c) complin and d) compsech. For all four pulses, we chose $t_{inv}=60\mu s$ and a maximum rf-field intensity of $\nu_{1,\text{max}}=100\text{kHz}$. For sech, complin and compsech, the sweepwidth SW was of 200 kHz whereas of 754 kHz for WURST.
Figure 3.14: Plot showing the function $Y(\Omega)$ as defined in Equation 3.41 for the four different pulses: hyperbolic secant and WURST where, as expected, no dip is observed, and compsech and complin with the dip on-resonance characteristic of the polarization-echo formation. From the figure, we see that the function $\theta(t)$ used to construct compsech fulfills Equation 3.41 a little less than the one for complin, but we will see in the following that both can lead to the formation of polarization echoes.
In this section, we verify numerically the concept of compensated pulse using the GAMMA environment. The length of all inversion pulses $t_{\text{inv}}$ is 60 $\mu$s. The amplitude and phase are discretized into 200 elements, corresponding to a time increment of 0.3 microsecond, during which the Hamiltonian has been assumed constant when numerically integrating the Liouville-von Neumann equation (see Subsection 2.2.6). For the powder averaging, we use 100 crystallite orientations according to the Cheng scheme. We use a two-spins system $^{13}$C-$^{13}$C and neglect J-couplings and chemical-shift anisotropies. For the definition of the dipolar strength $d_{\text{CC}}/2\pi$ and isotropic chemical shift $\Omega$, please refer to Section 2.2. Using a chemical shift $\Omega$ means that we have $\Omega_1 = -\Omega/2$ and $\Omega_2 = +\Omega/2$ for spins 1 and 2 respectively. The dipolar coupling strength $d_{\text{CC}}/2\pi$ is chosen either as 2 kHz or 10 kHz. To compensate the chemical shifts, we use the strategy used in [52]: two adiabatic pulses, the second one being $\pi$-phase-shifted with respect to the first one (see Figure 3.15). As long as the adiabatic condition (Equation 3.17) is fulfilled the magnetization vector will be locked on the effective field axis. For spin packets with a chemical shift $\Omega$ we obtain a $\theta_{\text{CS}}$ less than $\pi/2$ in the middle of the sweep as shown in Figure 3.15b) (see also Equation 3.40). Figure 3.15c) shows the trajectory of the polarization and the effective during the second $\pi$-phase-shifted inversion pulse. The polarization is now locked along the negative effective-field direction (due to the $\pi$-phase-shift) and returns to its initial state along the $+z$-axis irrespective of any chemical-shift offset $\Omega$.

Polarization Transfer

In this subsection we analyze the polarization transferred from spin 1 to spin 2 in a two-spin $^{13}$C-$^{13}$C system. We start with an initial density matrix $\sigma = S_{z1} - S_{z2}$ and observe the evolution of each spin under the influence of two compensated pulses applied successively, the second one being $\pi$-phase-shifted with respect to the first one. The chosen initial density matrix represents a nonequilibrium polarization state which is mandatory to have a longitudinal mixing and thus to observe a polarization echo. Indeed, if we would start with an equilibrium state $F_z$ and that the adiabatic condition would be fulfilled throughout the sweep, the sum polarization $F_z$ would stay a constant of motion along the effective field and no polarization echo would could be observed. The relevant interactions are the dipolar couplings $d_{\text{CC}}$ (as defined in Equation 2.9) and the chemical shift of each spin. If the compensated pulses are efficient in suppressing the
Figure 3.15: Scheme used to compensate the chemical-shifts evolution: two successive adiabatic pulses (here WURST pulses), the second one being $\pi$-phase-shifted with respect to the first one lead to a cancellation of the chemical-shifts evolution. 

(a) amplitude and phase of the pulses 
(b) trajectories of the effective field (grey) and the polarization (black) during the first inversion. The polarization is locked along the effective field as long as the adiabatic condition is fulfilled. 
(c) The polarization is locked along the negative effective-field direction (due to the $\pi$-phase-shift) and returns to its initial state along the $+z$-axis irrespective of any chemical-shift offset $\Omega$. $t_{\text{inv}}$ represents the inversion time of one adiabatic pulse. Adapted from [52].
polarization transfer due to dipolar coupling, we should observe the formation of polarization echoes, the chemical shifts being removed by the second $\pi$-phase shifted pulse. By symmetry we expect two polarization echoes (see Section 3.2), one on resonance fulfilling Equation 3.16 when the effective field lies in the xy-plane, and one along the -z-axis fulfilling Equation 3.15 at the end of the inversion. To check the formation of the first polarization echo, we will plot, as a function of time, the function $(<S_{1x}>^2+<S_{1y}>^2)^{1/2}$, whereas the function $<S_{z1}>$ will be depicted to assess the formation of the second polarization echo. A full polarization echo in the transverse plane, in the middle of the pulse will be reached for $(<S_{1x}>^2+<S_{1y}>^2)^{1/2}=1$, while a full polarization echo along the -z-axis, at the end of the inversion is formed when $<S_{z1}>=-1$.

Because we simulate two inversion pulses successively, we expect four polarization echoes, two polarization echoes in the transverse plane (at times $t=30$ and $90\,\mu$s), and two at the end of each inversion pulse (at times $t=60$ and $120\,\mu$s). Those times will be indicated by small black arrows in Figure 3.16 to Figure 3.20.

In Figure 3.16 we check the adiabaticity of the four pulses with a GAMMA simulation of an inversion on a two-spins $^{13}$C-$^{13}$C system without chemical shifts nor dipolar couplings. We plot the polarization evolution of the first spin $<S_{z1}>$ during two consecutive adiabatic inversions, the second one being $\pi$-phase-shifted with respect to the first one. All the four pulses are able to invert perfectly the polarization of the first spin both after the first inversion pulse and the second pulse. In Figure 3.16(a) the initial polarization $<S_{z1}>=1$ could thus be inverted to -1 after the first pulse, and finally back to the initial value of 1 after the second pulse. Also in Figure 3.16(b), all couplings and chemical shifts being absent, we can observe the full polarization echo in the transverse plane of the Bloch sphere, meaning the function $(<S_{1x}>^2+<S_{1y}>^2)^{1/2}$ reaches 1 for all the four pulses at the two expected times $t=30\,\mu$s and $60\,\mu$s. We note that some oscillations are present for the complin and WURST pulses but are absent for the sech and compsech pulses. Interestingly, the degree of oscillations observed in the polarization curves of Figure 3.16(a) seem to correlate directly with the residual coherences generated at the end of the first inversion at time $60\,\mu$s in Figure 3.16(b). We find indeed that the function $(<S_{1x}>^2+<S_{1y}>^2)^{1/2}$ which quantifies those coherences is highest for the complin and WURST pulses which exhibit the most oscillations. Without couplings nor chemical shifts, the only possible origin of those oscillations should be the fact that the angular sweeping rate $\dot{\theta}(r)$ is not sufficiently slower than the effect
field $\nu_{\text{eff}}$ or in other words that the Q is not high enough. Nevertheless, even with the presence of those oscillations, the inversion is almost perfect for all the four pulses.

Figure 3.17a) shows the evolution of the polarization on the first spin $\langle S_{z1} \rangle$ when chemical shifts are absent and setting the dipolar strength $d_{\text{CC}}/2\pi$ to 2 kHz. Figure 3.17b) shows the norm of the coherences $(\langle S_{1x} \rangle^2 + \langle S_{1y} \rangle^2)^{1/2}$ for the same parameters. After the second inversion, we get 100% polarization back on the first spin for both dipole-compensated pulses $\text{complin}$ and $\text{compsech}$, whereas we get about about 90% and 95% back for the $\text{sech}$ and $\text{WURST}$ pulses respectively. Concerning the norm of the coherences, we observe a small decay in the case of the $\text{sech}$ and $\text{WURST}$ pulses in the middle of the second inversion pulse, at $t=90\mu s$ whereas the full polarization echo is observed for both dipole-compensated pulses.

The situation is more marked when the larger dipolar coupling $d_{\text{CC}}/2\pi=10$ kHz is used, again without chemical shift, as depicted in Figure 3.17c) and d) for $\langle S_{z1} \rangle$ and $(\langle S_{1x} \rangle^2 + \langle S_{1y} \rangle^2)^{1/2}$ respectively. We observe again full polarization echoes in the middle ($t=30\mu s$ and $90\mu s$ in Figure 3.17c) and at the end ($t=60\mu s$ and $120\mu s$ in Figure 3.17d) of both $\text{complin}$ and $\text{compsech}$ inversion pulses. On the other hand, the two other adiabatic pulses $\text{sech}$ and $\text{WURST}$ are not able to properly invert the polarization at $t=60\mu s$ and consequently also after the second inversion at $t=120\mu s$ (Figure 3.17c)). Furthermore, the norm of coherences $(\langle S_{1x} \rangle^2 + \langle S_{1y} \rangle^2)^{1/2}$ do not reach 1 when the effective field lies in the xy-plane of the Bloch sphere, neither at time $t=30\mu s$ nor $t=90\mu s$ (see Figure 3.17d).

Figure 3.18 and Figure 3.19 depict the same GAMMA simulations as in Figure 3.17, but this time with chemical shifts of 5 kHz and 10 kHz respectively. With a chemical shift $\Omega$ of 5 kHz, the results are almost identical as the ones of Figure 3.17 computed without chemical shift with a dipolar coupling $d_{\text{CC}}/2\pi$ of 2 kHz (Figure 3.18a) and b)) as well as with a dipolar coupling of 10 kHz ((Figure 3.18c) and d)). In Figure 3.19a) and b), the polarization curves for $\langle S_{z1} \rangle$ and $(\langle S_{1x} \rangle^2 + \langle S_{1y} \rangle^2)^{1/2}$ respectively, obtained when the chemical shift $\Omega$ is set to 10 kHz and the dipolar strength $d_{\text{CC}}/2\pi$ to 2 kHz, are again very similar to Figure 3.17a) and b) and Figure 3.18a) and b). However, in Figure 3.19d) when $\Omega=10$ kHz and $d/2\pi=10$ kHz, compared to Figure 3.17d) and Figure 3.18d), we notice an increase in the function $(\langle S_{1x} \rangle^2 + \langle S_{1y} \rangle^2)^{1/2}$ at
3.4 GAMMA Simulations

t=90 μs in the case of \textit{sech} and \textit{WURST} reaching 43 % and 50 % respectively. On the other hand, the value of the same function, which was always almost 1 at \( t=90 \mu s \) in Figure 3.17d) and Figure 3.18d) amounts now to about 99 % for both \textit{complin} and \textit{compsech}.

Finally, in Figure 3.20 we computed again the polarization \( \langle S_{z1} \rangle \) and norm of coherences \( (\langle S_{1x} \rangle^2 + \langle S_{1y} \rangle^2)^{1/2} \) evolution as a function of time as in Figure 3.17 but with a chemical shift \( \Omega \) of 16 kHz. This large chemical shift difference seems more favorable for the standard \textit{sech} and \textit{WURST} pulses which are again able to invert properly the polarization when a dipolar strength \( d_{CC}/2\pi \) of 2 kHz is used (see Figure 3.20a)). We observe also that the function \( (\langle S_{1x} \rangle^2 + \langle S_{1y} \rangle^2)^{1/2} \) reaches almost 1 for the four pulses at times \( t=30 \mu s \) and \( t=90 \mu s \) (see Figure 3.20b)). This case is similar to the weak-coupling limit with \( \Omega \gg d_{CC} \) where the large chemical-shift differences \( \Omega \) truncates the planar (or flip-flop) terms of the homonuclear dipolar Hamiltonian \( H_{SS} \) (see Equation 2.10) leading to Ising terms of the form \( 2S_{1z}S_{2z} \). Indeed, if the adiabatic condition is sufficiently fulfilled, the chemical-shift-truncated dipolar interaction will commute with the effective field throughout the sweep and the homonuclear dipolar evolution will thus be effectively quenched. In this context, we could note that the idea of reintroducing the chemical shifts into a strongly-coupled homonuclear network to obtain a weakly-coupled one has been recently proposed as a solution to the problem of dipolar truncation [66] [67]. On the other hand, the strongly-coupled character of the homonuclear interaction gets larger in Figure 3.20c) and d) where a dipolar strength of \( d_{CC}/2\pi=10 \) kHz has been used. In this case, the dipole-compensated pulses are able to invert the polarization to -97 %, while the inversion reaches only -60 % and -70 % in the case of \textit{sech} and \textit{WURST} respectively. However, the function \( (\langle S_{1x} \rangle^2 + \langle S_{1y} \rangle^2)^{1/2} \) reaches only 98 % and 96 % at times \( t=30 \mu s \) and \( t=90 \mu s \) for the dipole-compensated pulses (see Figure 3.20d)). On the other hand, the large chemical shift of 16 kHz clearly helps the \textit{sech} and \textit{WURST} pulses to recover the norm of the coherences \( (\langle S_{1x} \rangle^2 + \langle S_{1y} \rangle^2)^{1/2} \) during the second inversion pulse upto 75 % compared to the lower value of 15 % in Figure 3.18d).

Thus, the GAMMA simulations presented in this section proved that the concept of \textit{theta-averaging} is a valid alternative to compensate the homonuclear dipolar evolution of a nonequilibrium polarization state even if chemical shifts are present, fact which is not necessarily true...
Figure 3.16.: Evolution of the polarization on spin 1 $<S_{z1}>$ as a function of time in a two-spins system without chemical shifts nor dipolar coupling. The rf-field intensity on resonance $\nu_{1,\text{max}}$ was set to 100 kHz. For the sech, compsech and complin pulses we used a sweepwidth SW of 200 kHz whereas we chose a sweepwidth of 754 kHz for the WURST pulse. Two adiabatic inversions of 60 $\mu$s are applied successively, the second one being $\pi$-phase-shifted with respect to the first one to remove the chemical-shifts evolution. The small black arrows indicate the location of the expected polarization echoes. a) polarization evolution of the first spin $<S_{z1}>$ as a function of time b) function $\sqrt{<S_{1x}^2> + <S_{1y}^2>}$ as function of time. As expected, without chemical shifts nor dipolar coupling, we obtain full polarization echoes in the transverse plane as well as at the end of both inversion.

when using standard adiabatic pulses like sech or WURST pulses.

3.5. Use of Dipole-compensated Pulses as C-Element in TOBSY sequences

In this section, we propose an application of the dipole-compensated pulses for use in TOBSY sequences of the type $\text{CN}_n^\nu_1$ (see Chapter 2). We first form a C-element as the concatenation of two complin pulses, the second one being $\pi$-phase-shifted with respect to the first one, or in short $(\text{complin})i(\text{complin})$. As a comparison, we form also a C-element of the form W$\text{W}$ as in
3.5 Use of Dipole-compensated Pulses as C-Element in TOBSY sequences

Evolution of the polarization on spin 1 \(<S_{z1}>\) as a function of time in a two-spins system without chemical shift. The rf-field intensity on resonance \(\nu_{1,\text{max}}\) was set to 100 kHz. For the sech, compsech and complin pulses we used a sweepwidth SW of 200 kHz whereas we chose a sweepwidth of 754 kHz for the WURST pulse. Two adiabatic inversions of 60 \(\mu\)s are applied successively, the second-one being \(\pi\)-phase-shifted with respect to the first one to remove the chemical-shifts evolution. The small black arrows indicate the location of the expected polarization echoes. a) polarization evolution of the first spin \(<S_{z1}>\) with \(d_{CC}/2\pi=2\) kHz. b) function \(\sqrt{<S_{1x}>^2 + <S_{1y}>^2}\) with \(d_{CC}/2\pi=2\) kHz c) polarization evolution of the first spin \(<S_{z1}>\) with \(d_{CC}/2\pi=10\) kHz d) norm of the coherences of the first spin \(\sqrt{<S_{1x}>^2 + <S_{1y}>^2}\) with \(d_{CC}/2\pi=10\) kHz
Figure 3.18.: Evolution of the polarization on spin 1 $\langle S_{z1} \rangle$ as a function of time in a two-spins system with a chemical shift of 5 kHz. The rf-field intensity on resonance $\nu_{1, \text{max}}$ was set to 100 kHz. For the sech, compsech and complin pulses we used a sweep with SW of 200 kHz whereas we chose a sweepwidth of 754 kHz for the WURST pulse. Two adiabatic inversions of 60 $\mu$s are applied successively, the second-one being $\pi$-phase-shifted with respect to the first one to remove the chemical-shifts evolution. The small black arrows indicate the location of the expected polarization echoes. a)polarization evolution of the first spin $\langle S_{z1} \rangle$ with $d_{CC}/2\pi = 2$ kHz. b)function $\sqrt{\langle S_{1x} \rangle^2 + \langle S_{1y} \rangle^2}$ with $d_{CC}/2\pi = 2$ kHz c)polarization evolution of the first spin $\langle S_{z1} \rangle$ with $d_{CC}/2\pi = 10$ kHz d)norm of the coherences of the first spin $\sqrt{\langle S_{1x} \rangle^2 + \langle S_{1y} \rangle^2}$ with $d_{CC}/2\pi = 10$ kHz
3.5 Use of Dipole-compensated Pulses as C-Element in TOBSY sequences

Figure 3.19: Evolution of the polarization on spin 1 $<S_{1z}>$ as a function of time in a two-spins system with a chemical shift of 10 kHz. The rf-field intensity on resonance $\nu_{1,\text{max}}$ was set to 100 kHz. For the sech, compsech and complin pulses we used a sweepwidth SW of 200 kHz whereas we chose a sweepwidth of 754 kHz for the WURST pulse. Two adiabatic inversions of 60 $\mu$s are applied successively, the second-one being $\pi$-phase-shifted with respect to the first one to remove the chemical-shifts evolution. The small black arrows indicate the location of the expected polarization echoes. a) polarization evolution of the first spin $<S_{1z}>$ with $d_{CC}/2\pi=2$ kHz b) function $\sqrt{<S_{1x}>^2 + <S_{1y}>^2}$ with $d_{CC}/2\pi=2$ kHz c) polarization evolution of the first spin $<S_{1z}>$ with $d_{CC}/2\pi=10$ kHz d) norm of the coherences of the first spin $\sqrt{<S_{1x}>^2 + <S_{1y}>^2}$ with $d_{CC}/2\pi=10$ kHz
Figure 3.20.: Evolution of the polarization on spin 1 \( <S_{1z}> \) as a function of time in a two-spins system with a chemical shift of 16 kHz. The rf-field intensity on resonance \( \nu_{1,\text{max}} \) was set to 100 kHz. For the sech, compsech and complin pulses we used a sweepwidth of 200 kHz whereas we chose a sweepwidth of 754 kHz for the WURST pulse. Two adiabatic inversions of 60 \( \mu s \) are applied successively, the second one being \( \pi \)-phase-shifted with respect to the first one to remove the chemical-shifts evolution. The small black arrows indicate the location of the expected polarization echoes. 

- **a)** polarization evolution of the first spin \( <S_{1z}> \) with \( \frac{d_{CC}}{2\pi}=2 \text{kHz} \) 
- **b)** function \( \sqrt{<S_{1x}^2> + <S_{1y}^2>} \) with \( \frac{d_{CC}}{2\pi}=2 \text{kHz} \) 
- **c)** polarization evolution of the first spin \( <S_{1z}> \) with \( \frac{d_{CC}}{2\pi}=10 \text{kHz} \) 
- **d)** norm of the coherences of the first spin \( \sqrt{<S_{1x}^2> + <S_{1y}^2>} \) with \( \frac{d_{CC}}{2\pi}=10 \text{kHz} \)
with two WURST pulses, again the second one shifted in phase by $\pi$ with respect to the first one. In the following, both sequences $(\text{complin})_i(\text{complin})_{91_{24}}$ and WiW$^1_{924}$ will be compared first experimentally and then numerically.

Note that the dipole-compensated pulses $\text{complin}$ and $\text{compsech}$ have been derived assuming a static sample. In the case of magic-angle spinning however, the spatial part of the dipolar interaction becomes time-dependent and contains modulations at frequencies $\pm \nu_r$ and $\pm 2 \nu_r$. This basically means that the theoretical derivations of $\text{complin}$ and $\text{compsech}$, carried out in Subsection 3.3.3 and Subsection 3.3.4 respectively, are only valid in the slow-spinning regime with $\nu_r \ll 2/t_{inv}$ with $t_{inv}$ the inversion time of the pulse and the factor 2 takes into account the fact that the first polarization echo is formed already after $t_{inv}/2$ in the transverse plane. When the MAS and polarization-echo formation timescales become comparable, interference effects come into play and a more involved theoretical treatment is in order, for instance a Floquet treatment. In the case of the $(\text{complin})_i(\text{complin})_{91_{24}}$ which will be used in the following, we have 18 $\text{complin}$ pulses, and consequently 36 polarization echoes, spanning 24 rotor periods. Thus, in this case, the rate of polarization-echoes formation is 1.5 times higher than the magic-angle spinning frequency. Although we are not completely in the slow-spinning regime, we nevertheless tried the $(\text{complin})_i(\text{complin})_{91_{24}}$ sequence to see if some improvement over the WiW$^1_{924}$ sequence could be observed.

Figure 3.21 depicts the pulse sequence used to assess experimentally the efficiency of a TOBSY sequences $CN^\nu_n$ with two different C-elements $(\text{complin})_i(\text{complin})$ (Figure 3.21a)) as well as WiW(Figure 3.21b)). We start by a cross-polarization from the proton bath to the carbons. We use the adiabatic-passage Hartmann-Hahn cross polarization[46]. On the $^{13}$C-channel, we first generate a nonequilibrium polarization state described by the density operator $\sigma = I_{z1}$ using a $90^\circ$ selective pulse on the spin 2 of a two-spins system. The coherences thus generated vanish away after the $z$-filter of duration $\tau_z$. The mixing block consists in the symmetry-based sequence $CN^\nu_n$ while using an off-resonance CW-decoupling on the proton channel (52). Finally the FID is acquired after the last $\pi/2$ reading pulse under XiX-decoupling.

In Figure 3.22a) we show the experimental transfer obtained for 2,3-$^{13}$C-sodium propionate on
Figure 3.21.: Pulse sequence used to measure homonuclear through-bond polarization transfer. We start by APHH-cross polarization \cite{10}. Afterwards, a selective pulse, followed by a z-filter, generate an initial density operator $\sigma_0 = I_{z1}$ for the 2-spin system used. The mixing sequence consists of $k$ basic blocks. Each block contains 9 C-Elements spanning 24 rotor periods. Each C-Element is phase-shifted by $2\pi/9$ with respect to the previous one. The C-Elements used here are a) the concatenation of two WURST pulses, the second one being $\pi$-phase-shifted with respect to the first one or WiW and b) the concatenation of two complin pulses, the second one $\pi$-phase-shifted with respect to the first one or (complin)$i$(complin).
3.5 Use of Dipole-compensated Pulses as C-Element in TOBSY sequences

a Varian Infinity+ 300 MHz spectrometer using a 2.3 mm rotor. The sweeping width $SW$ was 200 kHz for the $complin$ pulses and 754 kHz for the $WURST$ pulses. The maximum rf-field intensity $\nu_{1,\text{max}}$ was set to 100 kHz for both pulses. The inversion time $t_{\text{inv}}$ was 59.68 $\mu$s, the MAS frequency was set to 22.34 kHz. The polarization was transferred from the C$_{\alpha}$ to the C$'$. The protons off-resonance CW-decoupling during the mixing time was critical in obtaining a good transfer. We found experimentally that for a rf-decoupling field intensity of 160 kHz, an offset of 198.5 kHz was optimal to obtain a maximum transferred polarization for a fixed mixing time of 9.8 ms and was used for both the WiW9$_{24}$ and the $(complin)i(complin)9_{24}$ sequences. The blue and red circles represent the transferred polarization $<S_{z2}>$ (C$'$) for the WiW9$_{24}$ and the $(complin)i(complin)9_{24}$ sequences respectively. Experimentally, we observe a higher transferred polarization for the $(complin)i(complin)9_{24}$ sequence, reaching about 46% at 12 ms compared to WiW9$_{24}$ where the maximum transferred polarization amounts to about 31% at 10 ms. We thus observe a 15% enhanced polarization transfer with the TOBSY sequence based on the dipole-compensated pulse $complin$. The blue and red crosses depict the sum polarization $F_z = S_{z1} + S_{z2}$ for the WiW9$_{24}$ and the $(complin)i(complin)9_{24}$ sequences respectively. This sum polarization should ideally be a constant of motion. In our case, we observe a fast decay of the sum polarization which may be due to interference between the proton decoupling field and the inversion pulses. Moreover, in the case of the TOBSY sequence with $WURST$ pulses, we observe a not-understood oscillation of both the transferred polarization and the sum polarization, with marked minima at around 5 ms and 12 ms.

In Figure 3.22a) we plot a GAMMA$_{37}$ simulation of a four-spins model system: C$_2$C$^1$H$^1$H$^2$ with the parameters given in Table 3.1. We obtain a maximum transferred polarization at a mixing time $t_{\text{mix}} = 10$ ms for both sequences. The maximum transferred polarization for WiW9$_{24}$ reaches about 60% whereas the one for $(complin)i(complin)9_{24}$ reaches about 75%. We thus find that, in agreement with the experimental data from Figure 3.22a), the $(complin)i(complin)9_{24}$ sequence leads to a 15% higher transfer. Furthermore, the GAMMA simulation is able to reproduce the first minimum of the oscillation for the WiW9$_{24}$ sequence. The origin of that oscillation is unclear, but may be due to second-order Hartmann-Hahn recoupling between carbons and protons.
In Figure 3.23 we study numerically the influence of the offset of the proton off-resonance CW-decoupling on the polarization transfer. Using again the four-spins model system $^{13}C^2C^1H^1H^2$, we fixed the decoupling intensity to 160 kHz and varied the offset in the range 0 to 500 kHz. Figure 3.23a) shows the transferred polarization $<S_{2z}>$ as a function of the offset $\Delta \nu$ and mixing time $t_{\text{mix}}$ for the WiW$^9_{24}$ sequence whereas Figure 3.23b) depicts the same plot in the case of the $(\text{complin})i(\text{complin})9^1_{24}$ sequence. In Figure 3.23c) we plot vertical slices out of Figure 3.23a) and Figure 3.23b) for a constant mixing time $t_{\text{mix}}=10$ ms. As can be seen, the transfer is always higher in the case of the dipole-compensated sequence. Besides, the $(\text{complin})i(\text{complin})9^1_{24}$ sequence exhibits much less resonance conditions compared to the WiW$^9_{24}$ sequence. Another strong point in favor of the dipole-compensated TOBSY sequence is shown in Figure 3.23d) for an offset $\Delta \nu=400$ kHz, where all resonance conditions are absent (see Figure 3.23c)), is the much marked J-oscillation obtained in the complin case as in the WURST case, probably meaning that the homonuclear dipole couplings are more efficiently averaged out in the former case. Indeed, having two polarization echoes pro complin pulse (see Section 3.2), this means that for a full TOBSY-block with 18 complin pulses, we have 36 polarization echoes spanning 24 rotor periods in the case of $(\text{complin})i(\text{complin})9^1_{24}$. This means that the rate of averaging homonuclear dipolar coupling is in our case 1.5 higher than MAS, thus explaining the higher efficiency of $(\text{complin})i(\text{complin})9^1_{24}$ compared to WiW$^9_{24}$.

To conclude, we have successfully implement the dipole-compensated adiabatic pulses complin in a TOBSY sequence and observed experimentally a 15% improved polarization transfer compared with the same sequence based on WURST pulses. The enhanced polarization transfer could also be fully confirmed numerically using GAMMA [37].

3.6. Conclusion

To sum up, dipole-compensated adiabatic inversion pulses with the property of averaging out homonuclear dipolar couplings have been introduced. We first derived analytically two different kind of compensated pulses based on the concept of theta-averaging, first a pulse based on a piecewise constant angular sweeping rate complin (Subsection 3.3.3), and second a pulse having a smoother function $\theta(t)$ and consequently better adiabatic properties compsech (Subsection 3.3.4).
Table 3.1.: Parameters of the four-spins system \( {^4C^2}{C^1}H^1H^2 \) used in the GAMMA simulations. The dipolar strength \( d/2\pi \) is defined in [Equation 2.9]. The internuclear distance \( r \) as well as the three Euler angles \( \alpha, \beta \) and \( \gamma \) are also given for each pair of nuclei. The J-coupling, and the isotropic chemical shift are given in natural frequency units. The parameters correspond to \( 2,3-^{13}C \)-sodium propionate at \( 300 \text{MHz} \).
a) Experimental transferred polarization from spin 1 (CH$_2$) to spin 2 (CH$_3$) in 2,3-$^{13}$C-sodium propionate using the sequences WiW$^{11}_{24}$ (blue circles) and (complin)i(complin)$^9_{24}$ (red circles). The sum polarization is denoted by the red and blue squares for (complin)i(complin)$^9_{24}$ and WiW$^{11}_{24}$ respectively. The experiment was carried out on a Varian Infinity+ 300 MHz with a 2.3 mm rotor. The MAS frequency $\nu_r$ was set to 22.3 kHz. The maximum rf-field intensity $\nu_{1,\text{max}}$ of both adiabatic inversions complin and WURST was set to 100 kHz and their inversion time $t_{\text{inv}}$ to 59.68 $\mu$s. The sweeping range $\text{SW}$ for the WURST pulse was set to 754 kHz whereas the one for the complin pulse was set to 200 kHz. An off-resonance CW-decoupling was used during the TOBSY mixing sequence with an rf-field intensity $\nu_{\text{H,dec}}$ of 160 kHz and an off-resonance offset of 198.5 kHz which was optimized experimentally. An XiX-decoupling scheme was used during the detection period with an rf-field intensity of 160 kHz. b) GAMMA$^{37}$ simulation using a four-spins model-system $C^2C^1H^1H^2$ with the parameters given in Table 3.1.
Figure 3.23: GAMMA numerical simulations using a four-spins system \( C^8C^3H^1H^2 \) with the parameters given in Table 3.1 modelling 2,3-\( ^{13} \)C-sodium propionate at a proton Larmor frequency of 300 MHz. Simulated transferred polarization on the second spin \( <S_{2z}> \) for off-resonance CW-decoupling with \( \nu_1,dec = 160 \text{kHz} \) as a function of the decoupling offset \( \Delta\nu \) and mixing time \( t_{mix} \) using a) \( \text{WiW}^1_{24} \) and b) \( \text{(complin)i(complin)}^1_{24} \) c) Slices out of a) and b) showing the transferred polarization for a constant mixing time \( t_{mix}=10 \text{ms} \) as a function of the decoupling offset \( \Delta\nu \). d) Slices of Figure 3.23a) and Figure 3.23b) showing the transferred polarization for a constant decoupling offset \( \Delta\nu=400 \text{kHz} \) as a function of the mixing time \( t_{mix} \). For that decoupling offset, away from any resonance condition (see Figure 3.23c)) we observe a more marked oscillatory behaviour for the \( \text{(complin)i(complin)}^1_{24} \) than for the \( \text{WiW}^1_{24} \) pulse sequence.
In Subsection 3.3.6, we first showed that the two derived dipole-compensated pulses lead indeed to a marked dip of the scaling factor $P_2(\cos \theta(t))$ averaged over an inversion time for on-resonance spin-packets (see Figure 3.14), whereas no such dip could be observed in the case of standard adiabatic inversion pulses \textit{sech} and \textit{WURST}. In Section 3.4, we then confirmed numerically the concept by checking the formation of polarization echoes in two-spin polarization transfer \textit{GAMMA} simulations during two inversion pulses applied successively, the second-one being $\pi$-phase-shifted with respect to the first one, in order to compensate chemical shifts. We studied the influence of the dipolar strength $d_{CC}/2\pi$ (2 kHz and 10 kHz) and of the chemical shifts $\Omega$ (0, 5, 10 and 16 kHz) on the polarization echoes formation. For an inversion time of 60 $\mu$s, a maximum rf-field intensity $\nu_{1,\text{max}}$ and a sweepwidth $SW=200$ kHz we obtain almost 100\% inversion of the first spin after the second inversion pulse ($t=120$ $\mu$s) in all cases, except in the last case with $d_{CC}=10$ kHz and $\Omega=16$ kHz where we got about 92\% and 94\% back-inverted polarization for the \textit{complin} and \textit{compsech} pulses respectively. The standard adiabatic inversion pulses \textit{sech} and \textit{WURST} were, in all cases simulated here, less efficient in inverting the non-equilibrium polarization state. Interestingly, we note that for $\Omega=16$ kHz and $d_{CC}=2$ kHz (see Figure 3.20), their efficiency is quite comparable to the dipole-compensated pulses, the inversion being almost perfect. This case is very close to the weak-coupling limit with $\Omega \gg d_{CC}$ where the large chemical shift differences $\Omega$ truncates the planar (or flip-flop) terms of the homonuclear dipolar Hamiltonian $H_{SS}$ (see Equation 2.10), thus generating an Ising Hamiltonian of the form $S_z^1 S_z^2$. Indeed, if the adiabatic condition is sufficiently fulfilled, the Ising Hamiltonian will commute with the effective field throughout the sweep and the homonuclear dipolar evolution will thus be effectively quenched. In this context, we could note that the idea of reintroducing the chemical shifts into a strongly-coupled homonuclear network to obtain a weakly-coupled one has been recently proposed as a solution to the problem of dipolar truncation [66][67].

We also observed, as expected, the formation of full polarization echoes when the effective lies along the xy-plane in all cases, except for the cases $d_{CC}=10$ kHz and $\Omega=10$ kHz with a polarization echo of about 98\% for both \textit{complin} and \textit{compsech} at $t=90$ $\mu$s and for $d_{CC}=10$ kHz and $\Omega=16$ kHz with polarization echoes of about 92\% and 95\% for \textit{complin} and \textit{compsech} respectively. Again, except in the case $d_{CC}=2$ kHz and $\Omega=16$ kHz where all the pulses, standard pulses \textit{sech} and \textit{WURST} as well as dipole-compensated pulses \textit{complin} and \textit{compsech} have about the
same efficiency and lead to an almost full polarization echo in the transverse plane \(t=90 \mu s\), the dipole-compensated pulses exhibit in all cases simulated almost 100% polarization echoes in the transverse plane.

Finally, in Section 3.5, we presented a possible application of the dipole-compensated adiabatic inversion \textit{complin} as a C-element in a TOBSY sequence. We thus compared the polarization transfer from the \(C\alpha\) to the carbonyl in 2,3-\textsuperscript{13}C-sodium propionate using the sequence \((\textit{complin})i(\textit{complin})9\)\textsubscript{24} and compared it with the sequence \(\text{WiW9}_{24}\) using \textit{WURST} pulses. For proton decoupling during the mixing time, we used an off-resonance CW-irradiation. We obtained about 10% more transferred polarization with the \((\textit{complin})i(\textit{complin})9\)\textsubscript{24} sequence compared to \(\text{WiW9}_{24}\). This can be explained by the fact that the \((\textit{complin})i(\textit{complin})9\)\textsubscript{24} sequences generate 36 polarization echoes over 24 rotor periods, leading to enhanced homonuclear dipolar coupling suppression compared to \(\text{WiW9}_{24}\). A GAMMA\textsuperscript{37} simulation based on a four-spin system \(C^2C^1H^1H^2\) was able to reproduce the 10% enhanced polarization transfer.

3.7. Outlook

First, those dipole-compensated adiabatic inversion pulses try to conciliate two different aspects. On the one hand, the broad-band aspect of any adiabatic inversion which should lead to perfect population inversion over the largest possible chemical-shift range. On the other hand, the narrow-banded aspect of the polarization echo formation of a homonuclear network of spins which requires a narrow chemical-shift range. As seen in this work, we showed numerically that it should be possible to invert almost completely a nonequilibrium polarization state for chemical-shifts up to 10 kHz and dipolar strength \(d_{CC}=10\) kHz. In this context, we may cite the work of Dong et al.\textsuperscript{68} who used the experimental \(\pi\)-pulse imperfections to generate full magic echoes over about the chemical shift range of 8 kHz on a static \textsuperscript{29}Si sample.

Second, we may say that those pulses lead to better inversion only in cases with longitudinal mixing and an active homonuclear dipolar evolution, as for example, in polarization transfer experiments. Indeed, those pulses are not foreseen to lead to better inversions for equilibrium population inversion. If the adiabaticity condition is well fulfilled, the magnetization vector should always lie along the effective field and consequently be a constant of motion, meaning
that no echo formation is possible as no evolution is present.

Third, although the TOBSY experiment of [Section 3.5] were carried out using off-resonance CW-decoupling, other proton-decoupling schemes are possible as well. For instance, we may try XiX-decoupling as was done in [Section 2.7] We could also check if the good decoupling conditions $\nu_{m,XiX} = \nu_r$ still works with adiabatic pulses. However, as the rf-field intensity is not constant in a symmetry-based sequence with adiabatic inversions, we cannot apply the very efficient XiX-decoupling with $\nu_{m,XiX} = \nu_{1S}$ anymore. On the other hand, we may also try symmetry-based decoupling sequences as has been done in [Chapter 2]. To conclude, as the proton homonuclear dipolar couplings (for instance about 45 kHz in CH$_2$ groups) are often comparable to or larger than MAS frequencies, we could as well imagine a sequence based on dipole-compensated pulses to help MAS in averaging out those interactions. A final point may be to analyse in detail the behaviour of the compensated pulses under magic-angle spinning using a more involved theoretical treatment valid also outside the slow-spinning regime. For instance, in the context of C-sequences relevant to [Section 3.5] we may consider a trimodal Floquet approach with the three basic frequencies $\nu_{1I}$ (in the case of CW-decoupling on protons), the MAS spinning frequency $\nu_r$ and the modulation frequency $\nu_m = 1/\tau_m$ stemming from the symmetry-based sequence $CN^\nu_n$ with $\tau_m$ the duration of N consecutive C-elements.
4. Conclusion

In Chapter 1 we have presented a powerful full-wave solver for CPW-microcoil resonators based the mixed-potential integral equation (MPIE). This model contains Ohmic losses as well as dielectric and radiation losses. The information of the stratified medium is contained in the Green’s functions which are the kernels of the MPIE. They are evaluated only once at the beginning of each optimisation run. The Moment Matrix could also be mapped into a very efficient algorithm avoiding the evaluation of redundant terms. The time gained with this strategy is considerable compared to standard FDTD softwares which are extremely time-consuming for optimization purposes (factor gained up to 50). With the solver developed, we have studied different microcoil resonators based on coplanar technology (CPW). The spin sensitivity of such a sensor is directly proportional to the magnetic field intensity generated in the loop for a fixed source power. To this end, we computed the normal component of the magnetic field intensity of eight different resonators, four $\lambda/2$- and four $\lambda/4$-resonators. We found the $\lambda/4$-resonators maximum field intensity is a bit less compared to the $\lambda/2$-resonators for the same excitation. This may be due to a field inhomogeneity at the top-end of the $\lambda/4$-resonators as can be seen on the simulations.

Chapter 2 was concerned with the heteronuclear decoupling during rotor-synchronized symmetry-based sequences under magic-angle spinning. We first showed in Section 2.6 experimentally that a phase inversion supercycled version of a PC9 sequence was able to improve the polarization transfer by about 10% using CW-decoupling. This result was later on confirmed numerically on a four-spins system $\text{C}_2\text{C}_1\text{H}_1\text{H}_2$ using the GAMMA environment. In Section 2.7 we have demonstrated that an XiX-decoupling characterised by its amplitude $\nu_{1I}$ and its modulation frequency $\nu_{m,\text{XiX}}$ is a viable alternative to CW-decoupling. We first found experimentally the good decoupling condition, where the XiX-modulation frequency equals the MAS spinning frequency, $\nu_{m,\text{XiX}}=\nu_r$. This special condition could lead to an enhanced magnetization transfer.
compared to CW-decoupling at a relatively strong rf-field intensity ($\nu_1 \geq 190$ kHz), while being quite inefficient at lower intensities. This result could also be fully confirmed numerically. Afterwards, increasing the modulation frequency $\nu_{\text{m,XiX}}$, we found that when the XiX-modulation frequency equals the rf-field intensity used on the S spins channel (here $^{13}C$) namely $\nu_{\text{m,XiX}} = \nu_{1S}$ a noticeable increase in polarization transfer could be observed, even at lower decoupling-field intensity. A GAMMA$^{37}$ simulation was able to reproduce quantitatively this condition. In Section 2.8 we noticed that the condition $\nu_{\text{m,XiX}} = \nu_{1S}$ could be expressed in two different manners using a dual-channel symmetry based notation. First, by defining a C-element as the juxtaposition of two rectangular pulses L of arbitrary flip-angle, the second one being $\pi$-phase-shifted with respect to the first one, we got $\nu_{\text{m,XiX}} = \nu_{1S} \equiv \text{PC9}_6^1\text{L18}_6^0$. Second, with a rectangular pulse L of arbitrary flip angle instead of a C-element (we call the sequence so formed, a L-sequence), we obtained: $\nu_{\text{m,XiX}} = \nu_{1S} \equiv \text{PC9}_6^1\text{L36}_6^1$. Using Levitt’s Mathematica package$^{36}$, we selected 185 Sequences with z-rotation leading to the minimum number of 7 symmetry-allowed terms in the average Hamiltonian. We did the same without z-rotation, i.e. with the symmetry number $\nu$ set to zero, and obtained 10 sequences. The sequences with z-rotation were all tested numerically for the C-sequences and for the L-sequences, whereas the sequences without z-rotation were tested for the C-sequences only. The common trait of all the dual channel symmetry based sequences is the smoother behaviour with respect to the decoupling field rf amplitude of the transferred polarization compared to CW-decoupling. We found many sequences having a higher transfer for the $\nu_1 \leq 150$ kHz region, that one being of importance for protein NMR to avoid sample degradation. We found especially the sequences PC9$^1_6$L18$^8_6$ and PC9$^1_6$L36$^1_6$ and their minus-$\nu$ counterparts PC9$^1_6$L18$^8_6$ and PC9$^1_6$L36$^1_6$ which appear very promising.

In Chapter 3 we introduced dipole-compensated adiabatic inversion pulses with the property of averaging out homonuclear dipolar couplings. We first derived analytically two different kind of compensated pulses based on the concept of theta-averaging, first a pulse based on a piecewise constant angular sweeping rate complin (Subsection 3.3.3), and second a pulse having a smoother function $\theta(t)$ and consequently better adiabatic properties compsech (Subsection 3.3.4). In Section 3.4 we could confirm the concept numerically with some GAMMA$^{37}$ simulations. We performed extensive polarization transfer simulations on a two-spin $^{13}C$-$^{13}C$ system by varying the dipolar strength $d/2\pi$ (2 and 10 kHz) and the isotropic chemical-shift $\Omega$
(0, 5, 10 and 16 kHz) and compared the efficiency of complin and compsech with the standard adiabatic inversions sech and WURST. The two dipole-compensated pulses outperformed the standard adiabatic pulses, leading to an almost perfect inversion for all cases simulated. Finally, in Section 3.5, we implemented the complin dipole-compensated pulse in the TOBSY sequence (complin)i(complin)i and obtained experimentally a 15% enhanced polarization transfer on 2,3-$^{13}$C-sodium propionate compared to WiW9_{24}. This enhancement could also be confirmed numerically using GAMMA37.
5. Outlook

The numerical study of Chapter 1 has shown that the magnetic field intensity generated inside the microcoil of both $\lambda/2$ and $\lambda/4$-resonators is of about the same order of magnitude, meaning that both types of resonators should lead to similar spin sensitivity. With the model developed in this work, it is an easy matter to back the opposite side of the dielectric by a ground plane by setting $R_{12}^{\text{TE}} = -1$ and $R_{12}^{\text{TM}} = 1$ as explained in Subsection 1.3.6, meaning microstrip- or CPW-grounded resonators could be studied as well. In this work, we used rectangular current cells for ease of implementation. When working with rounded shapes it may be advantageous to use triangular current cells (as in [17]). Finally, those resonators are foreseen to have applications in the fields of electron spin resonance as well as nanoelectronics, spintronics, and quantum information processing.

Further research along the line of Chapter 2 could be to try other form of decoupling, for instance the dual channel symmetry-based sequences derived in Section 2.8 with the supercycled version PSC$_9^{16}$ of Section 2.6 to see if the improved magnetization transfer could be maintained or reinforced. In order to verify the promising higher polarization transfer simulated with the sequences PC$_9^{16}$L$_{18,8}$ and PC$_9^{16}$L$_{36,17}$ and their minus-$\nu$ counterparts PC$_9^{16}$L$_{18,8}$ and PC$_9^{16}$L$_{36,19}$, those latter should be experimentally assessed on a spectrometer. From the results obtained in Chapter 2, we can conclude that the heteronuclear decoupling under magic angle spinning is a fully coherent process involving I and S spins, and that the assumption that “the I-spins are perfectly decoupled” is not always met in practice, especially with samples containing protons. One should therefore be cautious, when developing homonuclear sequences without taking care of the heteronuclear couplings. This work has shown that the many resonance conditions present when using CW-decoupling could be efficiently reduced by using dual-channel symmetry-based rotor-synchronised decoupling sequences for which the polarization transfer obtained is much smoother with respect to the decoupling-field intensity. Overall, we believe that the future of het-
eronuclear decoupling for high-resolution solid-state NMR, lies fully in the region $\nu_1 \leq 160 \text{kHz}$ relevant for protein NMR. In this context, we may cite the recent high-phase TPPM heteronuclear decoupling scheme\cite{53}, whose efficiency in this decoupling-field intensity range is due to the quenching of the rotary resonance (RR) conditions $\nu_1 = n \nu_r$ with $n=1,2$. As shown in this work, there is room for improvement in trying other phase- and/or amplitude-modulated decoupling schemes at moderate MAS frequency. Especially in the context of C/R sequences, as the symmetry-based theory tells nothing about the form of the basic elements, we believe there is room for improvement.

The dipole-compensated adiabatic inversion pulses introduced in Chapter 2 try to conciliate two different aspects. On the one hand, the narrow-banded aspect of the polarization-echo formation of a homonuclear network of spins which requires a narrow chemical-shift range and on the other the broad-band aspect of any adiabatic inversion which should lead to perfect population inversion over the largest possible chemical-shift range. As seen in this work, we showed numerically that it should be possible to invert almost completely a nonequilibrium polarization state for chemical-shifts up to 10 kHz and dipolar strength $d_{CC}=10 \text{kHz}$ using $\text{complin}$ and $\text{compsech}$ with $t_{\text{inv}}=60 \mu\text{s}$, $\nu_{1,\text{max}}=100 \text{kHz}$. and $SW=200 \text{kHz}$. Along this line, we may cite the work of Dong et al.\cite{68} who used the experimental $\pi$-pulse imperfections to generate full magic echoes over about the chemical shift range of 8 kHz on a static $^{29}\text{Si}$ sample. However, we may say that those pulses lead to better inversion only in cases where a longitudinal mixing with a polarization difference which will evolve under a dipolar Hamiltonian, as in polarization-transfer experiments. Indeed, those pulses are not foreseen to lead to better inversions for equilibrium population inversion. If the adiabaticity condition is well fulfilled, the magnetization vector should always lie along the effective field and consequently be a constant of motion, meaning that no echo formation is possible as no evolution is present. If this case, we may surmise that solely the adiabaticity factor $Q$, along with the condition that the effective field be greater than any interactions present in the system, will determine the efficiency of the inversion. Finally, although the TOBSY experiment of Section 3.5 were carried out using off-resonance CW-decoupling, other proton-decoupling schemes are possible as well. For instance, we may try XiX-decoupling as was done in Section 2.7. We could also check if the good decoupling conditions $\nu_{m,\text{XiX}} = \nu_r$ still works with adiabatic pulses. However, as the rf-field intensity is not constant in a symmetry-based sequence
with adiabatic inversions, we cannot apply the very efficient \( \text{XiX-decoupling with } \nu_{m,\text{XiX}} = \nu_{1S} \) anymore. On the other hand, we may also try symmetry-based decoupling sequences as has been done in Chapter 2. As a final word, as the proton homonuclear dipolar couplings (for instance about 45 kHz in CH\(_2\) groups) are often comparable to or larger than MAS frequencies, we could as well imagine a sequence based on dipole-compensated pulses to help MAS in averaging out those interactions. A last point could be to analyse thoroughly the behaviour of the compensated pulses under magic-angle spinning using a more involved theoretical treatment, like a multimodal Floquet approach\textsuperscript{[69]}, valid also outside the slow-spinning regime.
A. Derivation of the Potentials for coplanar configuration (CPW)

Here we rederive the vector and scalar potentials which are the kernels of the MPIE (Equation 1.30) suitable for CPW-configuration. In the spectral domain, the magnetic and electric fields generated by a x-directed Hertzian dipole are given respectively by

\[
\tilde{G}_{zx}^{H} = \frac{1}{4\pi}(1 + R^{TE})\frac{j k_y}{-j k_z} e^{-j k_z z} \quad (A.1)
\]

\[
\tilde{G}_{zx}^{E} = -\frac{j k_x}{4\pi \omega c j} (1 - R^{TM}) e^{-j k_z z} \quad (A.2)
\]

The normal derivative of the electric field, needed to derive the scalar potential reads:

\[
\frac{d}{dz} \tilde{G}_{zx}^{E} = \frac{(-j k_x)(-j k_z)}{4\pi \omega c j} (1 - R^{TM}) e^{-j k_z z} \quad (A.4)
\]

\[
= \frac{-k_x k_z}{4\pi \omega c j} e^{-j k_z z} (1 - R^{TM}) e^{-j k_z z} \quad (A.5)
\]

The Green’s function for the vector potentials \( G_{A}^{zx} \) is derived from the Green’s function for the normal magnetic field \( \tilde{G}_{zx}^{H} \) using Equation 37a) from Reference [5]:

\[
\tilde{G}_{A}^{zx} = -\frac{\mu_k G_{H}^{zx}}{j k_y} = \frac{1}{4\pi} \frac{(1 + R^{TE})}{j k_z} e^{-j k_z z} \quad (A.6)
\]
The Green’s function for the scalar potential $G_V$ is derived using Equation 48) of Reference [5]:

\[
\widetilde{G}_V = \frac{j\omega}{k^2} \left( \frac{d}{dz} \frac{G_{zx}}{j\kappa_x} \right) - \left( \frac{k}{k_p} \right)^2 \left( \frac{G_{zx}}{j\kappa_y e_0} \right)
\]
\[
(A.7)
\]

\[
= \frac{j\omega}{k^2} \left( \frac{-k_x k_z}{(j\kappa_x)(4\pi\omega e_0 j)} \right) \left( 1 - R^{TM} \right) - \left( \frac{k}{k_p} \right)^2 \left( \frac{1 + R^{TE}}{j\kappa_y e_0} \right) \frac{jk_y}{(-j\kappa_z)}
\]
\[
(A.8)
\]

\[
= \frac{1}{k^2_p} \left( \frac{-k_z (1 - R^{TM})}{j4\pi\epsilon_0} \right) - \left( \frac{k}{k_p} \right)^2 \left( \frac{1 + R^{TE}}{4\pi\epsilon_0(-j\kappa_z)} \right)
\]
\[
(A.9)
\]

\[
= \frac{-k^2_z (1 - R^{TM}) + k^2_p (1 + R^{TE})}{k^2_p 4\pi\epsilon_0 (+j\kappa_z)}
\]
\[
(A.10)
\]

\[
= \frac{1}{(4\pi\epsilon_0)(+j\kappa_z)} \left( k^2_p R^{TE} + k^2_z R^{TM} + k^2_0 - k^2_z \right)
\]
\[
(A.11)
\]

\[
= \frac{1}{(4\pi\epsilon_0)(+j\kappa_z)} \left( k^2_p R^{TE} + k^2_z R^{TM} + k^2_0 \right)
\]
\[
(A.12)
\]

\[
= \frac{1}{(4\pi\epsilon_0)(+j\kappa_z)} \left( \frac{k^2_p R^{TE} + k^2_z R^{TM}}{k^2_p} + 1 \right)
\]
\[
(A.13)
\]

\[
= \frac{1}{(4\pi\epsilon_0)(+j\kappa_z)} \left( \frac{k^2_p R^{TE} + k^2_z R^{TM}}{k^2_p} + 1 \right)
\]
\[
(A.14)
\]
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