Algorithmic Cooling of Spins by Optimal Control

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Algorithmic Cooling of Spins by Optimal Control

Research Thesis

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Abstract

Nuclear magnetic resonance (NMR) has proven to be a leading implementation of quantum information processors where each molecule in the sample constitutes a register of quantum bits (qubits) realized by spin half nuclei (hereinafter spins). The quantum logic gates are implemented by radio frequency waves transmitted on an ensemble of indistinguishable molecules, and by using the scalar coupling between the spins. The large number of molecules of the sample generates a detectable signal corresponding to the average state of the spin system.

At room temperature and under a constant and homogeneous magnetic field typical for NMR, the nuclear spins are in a highly mixed state. The probability of a spin to be aligned with the magnetic field is slightly higher than the probability of the spin to be aligned against the magnetic field - in terms of information theory, the Shannon entropy of the spin state is close to 1. Using data compression tools, the entropy of the spin system can be manipulated, effectively cooling some spins while heating others. However this closed-system technique is limited by Shannon’s entropy conservation on reversible operations.

Algorithmic cooling (AC) of spins counter intuitively utilizes opening the system to the heat bath as a method for cooling spins beyond Shannon’s bound. AC requires a spin system where some spins, called reset spins, thermalize significantly faster than other spins, called computation spins. Polarization compression or polarization exchange is applied to the spin system, manipulating some of the computation spins’ entropy to the reset spins, which quickly lose most of it to the environment. The process is similar to a heat engine and can be repeated, converging the system to a stable trajectory (limit-cycle) in the density-matrix space. The efficiency of AC is limited by the thermalization times ratios between the cooled computation spins and the reset spins.

In this work, multiple rounds of AC were applied on $^{13}\text{C}_2$-trichloroethylene (TCE), a three-spin system, at the Technion NMR lab, following the heat-bath cooling experiments conducted on TCE by my collaborators Mor, Elias, and Weinstein. We applied the first AC in liquid state NMR, in continuation of the pioneering AC experiment conducted in solid state NMR in 2005 by Baugh et al. The parameters of the Hamiltonian were measured from the spectrum and fed to GRAPE, an optimal control algorithm utilized to design efficient and robust radio frequency (RF) pulses required for AC.

Our main result is cooling a single spin by a factor of $4.61\pm0.02$ to $65\text{K}$, bypassing the Shannon bound for the system (4.22). The result matches the prediction of our simulation given the system parameters and the pulses’ efficiency. In a second experiment, focused on maximizing the information content (IC) of the two carbons, we measured polarizations of $3.78\pm0.02$ and $3.40\pm0.02$, with information content of $25.9\pm0.2$. In comparison, polarizations of $2.04\pm0.01$ and $2.93\pm0.01$ with IC $12.75\pm0.01$ were achieved in heat bath cooling applied in the previous work. Finally, in a third experiment aimed to maximize the IC of the entire molecule, we measured polarizations of $2.87\pm0.02$, $2.64\pm0.02$ for the carbons and $3.58\pm0.02$ for the proton, to yield an IC of $28.0\pm0.2$. In a heat bath cooling experiment with the same
goal conducted in the previous work, the two carbons and the proton spins were cooled by factors of
$1.74 \pm 0.01$, $1.86 \pm 0.01$ and $3.77 \pm 0.01$ respectively, reaching IC of $20.7 \pm 0.1$. 
# List of Notations and Abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mathbb{I}_n$</td>
<td>$n \times n$ identity matrix</td>
</tr>
<tr>
<td>$\langle \bullet \rangle$</td>
<td>Expectation value</td>
</tr>
<tr>
<td>$\dagger$</td>
<td>Hermitian adjoint</td>
</tr>
<tr>
<td>$B$</td>
<td>Magnetic field</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Gyromagnetic ratio</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>Product operator</td>
</tr>
<tr>
<td>$D1-D6$</td>
<td>Delays</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Chemical shift</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Polarization</td>
</tr>
<tr>
<td>$\varepsilon_{eq}$</td>
<td>Thermal equilibrium polarization</td>
</tr>
<tr>
<td>$\text{FT}(\bullet)$</td>
<td>Fourier transform</td>
</tr>
<tr>
<td>$h$</td>
<td>Reduced Plank’s constant</td>
</tr>
<tr>
<td>$H$</td>
<td>Hamiltonian</td>
</tr>
<tr>
<td>$H(\bullet)$</td>
<td>Shannon’s entropy</td>
</tr>
<tr>
<td>$I^{(i)}$, $I_1^{(i)}$, $I_2^{(i)}$</td>
<td>The angular momentum operators of the $i^{th}$ spin</td>
</tr>
<tr>
<td>$I^{(i)}$</td>
<td>The angular momentum vector of the $i^{th}$ spin</td>
</tr>
<tr>
<td>$\text{IC}$</td>
<td>Information content</td>
</tr>
<tr>
<td>$J$</td>
<td>Scalar coupling constant</td>
</tr>
<tr>
<td>$K_B$</td>
<td>Bolzmann’s constant</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density matrix</td>
</tr>
<tr>
<td>$\sigma_x, \sigma_y, \sigma_z$</td>
<td>Pauli matrices</td>
</tr>
<tr>
<td>$T_1$</td>
<td>Longitudinal relaxation time constant</td>
</tr>
<tr>
<td>$T_2$</td>
<td>Dephasing time constant</td>
</tr>
<tr>
<td>$U$</td>
<td>Unitary matrix</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>Target function</td>
</tr>
<tr>
<td>$[\phi]_\theta$</td>
<td>Rotation of a spin/qubit around $\hat{r}$</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Angular velocity</td>
</tr>
<tr>
<td>$\omega_L$</td>
<td>Larmor Frequency</td>
</tr>
</tbody>
</table>
## List of Notations and Abbreviations (Cont.)

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>3BC</td>
<td>3-bit compression</td>
</tr>
<tr>
<td>AC</td>
<td>Algorithmic cooling</td>
</tr>
<tr>
<td>CNOT</td>
<td>Control-NOT logic gate</td>
</tr>
<tr>
<td>CSWAP</td>
<td>Control-SWAP logic gate</td>
</tr>
<tr>
<td>Fib</td>
<td>Fibonacci algorithm</td>
</tr>
<tr>
<td>GRAPE</td>
<td>Gradient ascent pulse engineering</td>
</tr>
<tr>
<td>HS</td>
<td>Hilbert-Schmidt</td>
</tr>
<tr>
<td>IC</td>
<td>Information content</td>
</tr>
<tr>
<td>INEPT</td>
<td>Insensitive nuclei enhanced by polarization transfer</td>
</tr>
<tr>
<td>LSB</td>
<td>Least significant bit</td>
</tr>
<tr>
<td>MRI</td>
<td>Magnetic resonance imaging</td>
</tr>
<tr>
<td>MSB</td>
<td>Most significant bit</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>NMRQC</td>
<td>NMR quantum computing</td>
</tr>
<tr>
<td>NOC</td>
<td>Number of control points</td>
</tr>
<tr>
<td>NOT</td>
<td>Logic inversion gate</td>
</tr>
<tr>
<td>PAC</td>
<td>Practicable algorithmic cooling</td>
</tr>
<tr>
<td>PE</td>
<td>Polarization exchange</td>
</tr>
<tr>
<td>POTENT</td>
<td>Polarization transfer via environment thermalization</td>
</tr>
<tr>
<td>PPA</td>
<td>Partner pairing algorithm</td>
</tr>
<tr>
<td>PPS</td>
<td>Pseudo pure state</td>
</tr>
<tr>
<td>PT</td>
<td>Polarization transfer</td>
</tr>
<tr>
<td>RF</td>
<td>Radio frequency</td>
</tr>
<tr>
<td>RPC</td>
<td>Reversible polarization compression</td>
</tr>
<tr>
<td>SIMPSON</td>
<td>An NMR software</td>
</tr>
<tr>
<td>TCE</td>
<td>Trichloroethylene</td>
</tr>
<tr>
<td>WAIT</td>
<td>Wait step</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

One of the major challenges in building a quantum computer is to coherently control a large quantum system well enough to perform an arbitrary quantum algorithm [22]. Nuclear magnetic resonance (NMR) offers an excellent test bed for developing techniques to control quantum systems. Applying a quantum algorithm in NMR requires RF pulses that manipulate the spin system through the various steps of the algorithm. In this work, a polarization exchange pulse was designed and implemented experimentally on a solution of $^{13}$C$_2$-TCE (trichloroethylene), a 3-qubit system. The pulse was designed by SIMPSON [5], originally an NMR simulation program, that was lately expanded to implement the optimal control algorithm GRAPE [42, 73].

1.1 Overview of Quantum Mechanics

In this section, partially taken from other sources [55, 78], we’ll provide some of the basic concepts of quantum mechanics. In quantum mechanics, a system is commonly represented by a normalized vector in Hilbert space called the state vector. The state vector contains the full information on the probability distribution of the results of all possible measurements of the system. A notation introduced by Dirac is often utilized to describe vectors and matrices in quantum mechanics. The “ket” notation, $|\psi\rangle$, represents a column state-vector, while the “bra”, $\langle \psi |$, represents the complex conjugate of $|\psi\rangle$. A product of bra and ket is either a scalar or a matrix, depending on the order of multiplication. The following equations illustrate the simplest quantum system, the qubit (quantum bit), represented by a two dimensional vector.

\[
|\psi\rangle = \begin{pmatrix}
\alpha \\
\beta
\end{pmatrix}
\]

(1.1)

\[
\langle \psi | = (\alpha^*, \beta^*)
\]

(1.2)

\[
\langle \psi | \psi \rangle = (\alpha^*, \beta^*) \cdot \begin{pmatrix}
\alpha \\
\beta
\end{pmatrix} = |\alpha|^2 + |\beta|^2
\]

(1.3)

With the normalization condition $|\alpha|^2 + |\beta|^2 = 1$;

\[
|\psi\rangle \langle \psi | = \begin{pmatrix}
|\alpha|^2 & \alpha \beta^* \\
\alpha^* \beta & |\beta|^2
\end{pmatrix}
\]

(1.4)
Some commonly used notations for states and bases are the following:

\[ |\uparrow\rangle = |0\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad |\downarrow\rangle = |1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \]  
(1.5)

\[ |+\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad |_-\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \]  
(1.6)

### 1.1.1 Measurements

Due to the probabilistic nature of quantum mechanics, if the state \( |\psi\rangle \) is measured, the outcome “0” is obtained with a probability \( |\alpha|^2 \) and the outcome saying “1” is obtained with a probability \( |\beta|^2 \). Physicists like to use “observables” for describing measurements. Observable quantities of particles are described by Hermitian (self adjoint) matrices. Given a state vector \( |\psi\rangle \), the expectation value of the observable \( A \) is given by:

\[ \langle A \rangle = \langle \psi | A | \psi \rangle. \]  
(1.7)

If \( |\psi\rangle \) is an eigenstate of \( A \) with an eigenvalue \( a \), the outcome is \( \langle A \rangle = \langle \psi | A | \psi \rangle = a \). More generally, if \( |\psi\rangle = \sum_i \alpha_i |\psi_i\rangle \) (with sum of the \( \alpha \)s square equal 1) where each of the \( |\psi_i\rangle \) is an eigenstate of \( A \) with (non-degenerate) eigenvalue \( a_i \), the expectation value of \( A \) is

\[ \langle A \rangle = \langle \psi | A | \psi \rangle = \sum_i |\alpha_i|^2 a_i. \]  
(1.8)

### 1.1.2 Time Evolution and Quantum Gates

In a closed system, the evolution of the state vector in time is determined by the **Schrödinger equation**:

\[ i\hbar \frac{d|\psi\rangle}{dt} = H|\psi\rangle \]  
(1.9)

where \( H \), called the **Hamiltonian**, is an Hermitian operator and \( \hbar \) is Planck’s constant. The solution to the equation is

\[ |\psi(t)\rangle = e^{-\frac{it}{\hbar}}|\psi(0)\rangle = U|\psi(0)\rangle. \]  
(1.10)

The unitary\(^1\) matrix \( U \) is called the **propagator** as it propagates the state vector in time. In terms of quantum information theory, \( U \) is called a **quantum gate**. For example, when choosing \( t = \pi \) and the Hamiltonian,

\[ H = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \]  
(1.11)

the propagator is:

\[ U = e^{-\frac{iHt}{\hbar}} = -i \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \]  
(1.12)

Note that \( U|0\rangle = -i|1\rangle \), and \( U|1\rangle = -i|0\rangle \), hence up to a global phase, \( U \) is a NOT gate. Other important quantum gates are the Hadamard gate

---

\(^1\)For all Hermitian matrix \( A \), \( e^{iA} \) is unitary.
\[ \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}, \]  

and the Pauli matrices:

\[ \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \]  

### 1.1.3 The Density Matrix

An alternative representation of a quantum system is the **density matrix**. That description has an advantage, since it allows a generalization of the state of a quantum system as we now explain.

The density matrix equivalence of a state-vector is:

\[ \rho_\psi = |\psi\rangle\langle\psi|. \]  

A system is said to be in a **pure state** if its state vector is known - there exists an observable \( A \) such that the known state vector is its non-degenerated eigenstate, and the measurement outcome is known with certainty. When only the distribution of the state vector of the system is known, the system is in a **mixed state**, and can’t be expressed as a state vector. However, the system can still be represented by a density matrix:

\[ \rho = \sum_j p_j |\psi_j\rangle\langle\psi_j|. \]  

Here \( p_j \) is the probability of the system to be in a state \( |\psi_j\rangle \). For example, the state \( |+\rangle \) is pure, while the state “50% at \( |0\rangle \) and 50% at \( |1\rangle \)” is completely mixed (c.m.):

\[ \rho_{+} = |+\rangle\langle+| = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \quad \rho_{\text{c.m.}} = \frac{1}{2} |0\rangle\langle 0| + \frac{1}{2} |1\rangle\langle 1| = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \]  

It is important to note that the decomposition of \( \rho \) in equation 1.16 is not unique for a mixed state, and infinitely number of ensembles may lead to the same density matrix. For instance:

\[ \rho_{\text{c.m.}} = \frac{1}{2} |0\rangle\langle 0| + \frac{1}{2} |1\rangle\langle 1| = \frac{1}{2} |+\rangle\langle+| + \frac{1}{2} |-\rangle\langle-| = \frac{1}{2} \mathbb{I}_2. \]  

Given a density matrix \( \rho \), the expectation value of observable \( A \) can be calculated using equations 1.7 and 1.16:

\[ \langle A \rangle = \text{tr} (A \rho). \]  

### 1.1.4 Bloch Sphere Representation of a Qubit

A general state vector of a qubit is:

\[ |\psi\rangle = \alpha|0\rangle + \beta|1\rangle \]  

where \( \alpha, \beta \) are complex and \( |\alpha|^2 + |\beta|^2 = 1 \). A general density matrix of a pure state is therefore
\[
\rho_\psi = |\psi\rangle\langle\psi| = (\alpha|0\rangle + \beta|1\rangle) \cdot (\alpha^*|0\rangle + \beta^*|1\rangle) = \begin{pmatrix}
|\alpha|^2 & \alpha\beta^* \\
\alpha^*\beta & |\beta|^2
\end{pmatrix}.
\] (1.22)

Similarly to any \(2 \times 2\) Hermitian matrix over the complex, \(\rho\) can be decomposed to four basis matrices - the identity matrix, and the three Pauli matrices.

\[
\rho_\psi = \frac{1}{2} \left[ (|\alpha|^2 + |\beta|^2) \cdot \mathbb{1} + (|\alpha|^2 - |\beta|^2) \cdot \sigma_x + 2Re(\alpha^* \beta) \cdot \sigma_x + 2Im(\alpha^* \beta) \cdot \sigma_y \right].
\] (1.23)

Recalling that \(|\psi\rangle\) is normalized, and substituting \(\alpha = \cos(\theta)e^{i\xi}, \beta = \sin(\theta)e^{i\phi}\), the coefficients of the Pauli matrices are:

\[
\begin{align*}
1 &= |\alpha|^2 + |\beta|^2 \\
r_x &= 2Re(\alpha^* \beta) = 2Re \left( \cos(\theta) \sin(\theta) e^{i(\phi - \xi)} \right) = \sin(2\theta) \cos(\phi - \xi) \\
r_y &= 2Im(\alpha^* \beta) = 2Im \left( \cos(\theta) \sin(\theta) e^{i(\phi - \xi)} \right) = \sin(2\theta) \sin(\phi - \xi) \\
r_z &= |\alpha|^2 - |\beta|^2 = \cos^2(\theta) - \sin^2(\theta) = \cos(2\theta).
\end{align*}
\] (1.24)

The dependency of \(\vec{r}\) on \(2\theta\) and \(\phi - \xi\) is similar to a representation of a normalized vector in spherical coordinates:

\[
|\vec{r}|^2 = r_x^2 + r_y^2 + r_z^2 = \cos^2(2\theta) + \sin^2(2\theta) \cdot \left[ \cos^2(\phi - \xi) + \sin^2(\phi - \xi) \right] = 1.
\] (1.25)

Hence the density matrix of a qubit in a pure state can be expressed as a vector on a unit sphere, called the Bloch sphere.

\[
\rho_\psi = \frac{1}{2} \left( \mathbb{1} + r_x \sigma_x + r_y \sigma_y + r_z \sigma_z \right) = \frac{1}{2} \left( \mathbb{1} + \vec{r} \cdot \vec{\sigma} \right).
\] (1.26)

In NMR, the pauli matrices are often replaced by the angular momentum operators \(I_x = \sigma_x/2, I_y = \sigma_y/2, I_z = \sigma_z/2\), and therefore:

\[
\rho_\psi = \frac{1}{2} \mathbb{1} + r_x I_x + r_y I_y + r_z I_z = \frac{1}{2} \mathbb{1} + \vec{r} \cdot \mathbb{I}.
\] (1.27)

A density matrix in a mixed state is in the convex of the set of density matrices in pure state (see equation 1.16). Therefore a qubit in a mixed state will be represented by a vector inside the Bloch sphere.

The evolution of the density matrix is determined by the Liouville-von Neumann equation, which is equivalent to Schrödinger’s equation:

\[
\frac{d\rho}{dt} = \frac{i}{\hbar} [\rho, H].
\] (1.28)

Each of the pure states composing the density matrix evolves independently, hence the time propagation of the density matrix is:

\[
\rho(t) = \sum_j p_j |\psi_j(t)\rangle\langle\psi_j(t)| = \sum_j p_j e^{-i\mu t} |\psi_j(0)\rangle\langle\psi_j(0)| e^{i\mu t} = e^{-i\mu t} \rho(0) e^{i\mu t}.
\] (1.29)
1.1.5 Multiple Qubit Representation

The combined state vector of two state vectors is their tensor product. For example:

\[ |0\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \]

\[ |01\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \otimes \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}. \]  

The same applies to density matrices:

\[ \rho_{A\cup B} = \rho_A \otimes \rho_B. \]

Any \(2^n \times 2^n\) unitary matrix is a valid \(n\)-qubits quantum gate. For example, the Control-NOT (CNOT) gate inverts the controlled qubit iff the control qubit is \(|1\rangle\):

\[
\text{CNOT} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}. \]

Another example is the Control-SWAP (CSWAP) gate that swaps the two controlled qubits iff the control qubit is \(|1\rangle\):

\[
\text{CSWAP} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \end{pmatrix}. \]

1.2 NMR in Solution - Theory

1.2.1 Evolution

The free Hamiltonian in the lab frame of spins in a solution under a constant magnetic field is the following:

\[ H_{0}^{\text{lab}} = \sum_{i} \hbar \omega_i I_z^{(i)} + \sum_{ij} \hbar J_{ij} \sigma_z^{(i)} \cdot \sigma_z^{(j)}. \]

Where:

- \( \omega_i \) is the Larmor frequency of the \(i\)th spin. It equals the \(-\gamma_i B_z\) where \(B_z\) is the local magnetic field near the spin and \(\gamma_i\) is the spin’s gyromagnetic ratio.

- \( I_z^{(i)} \) is the z-axis angular momentum operator of the \(i\)th spin, equals \( \mathbb{I}_{2^{i-1}} \otimes \sigma_z / 2 \otimes \mathbb{I}_{2^{n-i}}. \)

\(^2\)A multiple qubit system that can’t be represented as a tensor product of state vectors is said to be entangled.
• $J_{ij}$ is the scalar isotropic (J) coupling constant between the \(i^{th}\) and \(j^{th}\) spins.

• \(I^{(i)}\) is the vector of the angular momentum operators of the \(i^{th}\) spin (i.e., \(I_z^{(i)}, I_y^{(i)}, I_z^{(i)}\)). The scalar product \(I^{(i)} \cdot I^{(j)}\) equals \(I^{(i)}_x I^{(j)}_x + I^{(i)}_y I^{(j)}_y + I^{(i)}_z I^{(j)}_z\), in a slight abuse of notation.

Spin state control is done by transmitting an RF field at frequencies close to the Larmor frequency [47]. The difference between the Larmor frequencies of \(^{13}\text{C}\) and \(^1\text{H}\) spins is at least 3 orders of magnitude greater than the difference between the frequencies of homonuclear spins. Hence, each group of homonuclear spins is independently controlled by an RF field at or near the resonance frequencies of its spins. When the radio frequency equals the Larmor frequency, the spin is on resonance. It is easier to analyze the system when the coordinates of each spin in the density matrix are rotating by a frequency of the RF field manipulating it. This way, the RF field will appear static (i.e., will not oscillate). It is proven in appendix A that the free Hamiltonian in the rotating frame is:

$$H_0 = \sum_i \hbar \delta_i I_z^{(i)} + \sum_{ij \text{ homo.}} \hbar J_{ij} I^{(i)}_z I^{(j)}_z + \sum_{ij \text{ hetero.}} \hbar J_{ij} I^{(i)}_z I^{(j)}_z. \quad (1.36)$$

Where \(\delta_i\) is the chemical shift of the \(i^{th}\) spin - the frequency difference between its Larmor frequency and the radio frequency that manipulates it; and the \(J\) coupling term differs between homonuclear and heteronuclear spin pairs. Adding the RF term, the full Hamiltonian is:

$$H(t) = H_0 + H_{RF}(t) \quad (1.37)$$

$$H_{RF}(t) = \sum_i \hbar \gamma_i \left( u_x^{(i)}(t) I_x^{(i)} + u_y^{(i)}(t) I_y^{(i)} \right). \quad (1.38)$$

Where \(H_{RF}(t)\) is the time-dependent RF Hamiltonian, \(u_{x/y}^{(i)}(t)\) is the amplitude of the radio wave transmitted on the \(i^{th}\) spin, in the x/y axis (of the rotating frame). Homonuclear spins are controlled by the same RF field, so their corresponding amplitudes are identical. For example, given a molecule with a single spin; transmitting on the spin resonance yields the following Hamiltonian in the rotating frame:

$$H = \hbar \gamma \left( u_x(t) I_x + u_y(t) I_y \right). \quad (1.39)$$

A \(\pi/2\) rotation around the y axis is applied on the spin by transmitting RF field with magnetic amplitude \(u_y = B_1\), for duration \(t = \frac{\pi}{2B_1\gamma}\):

$$U = e^{-i \frac{\mu B_1}{\hbar} t} = e^{-i \frac{\pi}{2} \sigma_y} = e^{-i \frac{\pi}{4} \sigma_y}. \quad (1.40)$$

This rotation is denoted by \(\left[ \begin{array}{c} \uparrow \\ \frac{\pi}{2} \end{array} \right]_y\).

### 1.2.2 Signal Acquisition (Measurement)

The heart of the NMR spectrometer is the transceiver coil, aligned perpendicular to the principle magnetic field. In the lab frame, the spins precess around the z axis, and their net magnetization changes the magnetic flux, inducing a detectable current on the coil (Faraday's law). Utilizing a quadrature detection, two signals are extracted, proportional to the expectation values of \(I_x\) and \(I_y\) of the observed spins:

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The spectrum is calculated by taking the Fourier transform (FT) of the combined signal

\[
\hat{f}(\omega) = \text{FT}(\langle I_x(t) \rangle + i \langle I_y(t) \rangle) = \int_{-\infty}^{\infty} dt \cdot e^{-i\omega t} \text{tr}(\rho(t) I_\pm) \tag{1.42}
\]

\[
I_\pm = I_x + iI_y. \tag{1.43}
\]

The integral over the real part of the spectrum is proportional to \( \langle I_x \rangle \) at \( t=0 \), while the integral over the imaginary part is proportional to \( \langle I_y \rangle \) at \( t=0 \) (see proof at appendix B.1). A basic NMR experiment is to apply an excitation pulse, a \( \frac{\pi}{2} \) rotation, making the polarization visible in the spectrum. Since the polarization determines the signal, polarization enhancement techniques are highly sought out.

### 1.2.3 Thermal Equilibrium and the Initial State

The thermal energy at room temperature is much higher than the magnetic potential energy of nuclear spins even in the most advanced NMR devices. Therefore, at equilibrium, the qubit ensemble is in a very highly mixed state - the probability difference between the “up” and “down” states, namely the polarization \( \varepsilon \), is very small. Utilizing the Bolzmann distribution:

\[
\varepsilon_{eq} = P_{\uparrow}^{eq} - P_{\downarrow}^{eq} = \frac{1}{1 + e^{-\Delta E / k_B T}} - \frac{e^{-\Delta E / k_B T}}{1 + e^{-\Delta E / k_B T}},
\]

\[
\varepsilon_{eq} = \tanh \left( \frac{\Delta E}{2k_B T} \right)
\]

Here \( \gamma \) is the gyromagnetic ratio of the spin, \( B_z \) is the magnetic field, \( k_B \) is the Boltzmann constant, and \( T \) is the temperature. In the 600 Mhz NMR\(^3\), the polarization of protons and \(^{13}\)C is in the order of \(10^{-5}\). Spins with higher polarization than their equilibrium polarization are considered cool. The density matrix of a single spin at equilibrium polarization \( \varepsilon \) is:

\[
\rho = \begin{pmatrix}
\frac{1+\varepsilon}{2} & \frac{1-\varepsilon}{2} \\
\frac{1-\varepsilon}{2} & \frac{1+\varepsilon}{2}
\end{pmatrix} = \frac{1}{2} \mathbb{I} + \varepsilon I_z. \tag{1.45}
\]

The density matrix of two qubits (neglecting \( O(\varepsilon^2) \) terms) is:

\[
\rho = \left( \begin{pmatrix}
\frac{1+\varepsilon}{2} & \frac{1-\varepsilon}{2} \\
\frac{1-\varepsilon}{2} & \frac{1+\varepsilon}{2}
\end{pmatrix} \otimes \begin{pmatrix}
\frac{1+\varepsilon}{2} & \frac{1-\varepsilon}{2} \\
\frac{1-\varepsilon}{2} & \frac{1+\varepsilon}{2}
\end{pmatrix} \right) = \begin{pmatrix}
\frac{(1+\varepsilon)^2}{4} & \frac{(1+\varepsilon)(1-\varepsilon)}{4} & \frac{(1+\varepsilon)(1-\varepsilon)}{4} & \frac{(1-\varepsilon)^2}{4} \\
\frac{(1+\varepsilon)(1-\varepsilon)}{4} & \frac{(1+\varepsilon)^2}{4} & \frac{(1-\varepsilon)^2}{4} & \frac{(1-\varepsilon)(1+\varepsilon)}{4} \\
\frac{(1+\varepsilon)(1-\varepsilon)}{4} & \frac{(1-\varepsilon)^2}{4} & \frac{(1+\varepsilon)^2}{4} & \frac{(1+\varepsilon)(1-\varepsilon)}{4} \\
\frac{(1-\varepsilon)^2}{4} & \frac{(1-\varepsilon)(1+\varepsilon)}{4} & \frac{(1-\varepsilon)(1+\varepsilon)}{4} & \frac{(1+\varepsilon)^2}{4}
\end{pmatrix}. \tag{1.46}
\]

\(^3\)In NMR, the magnetic field is often measured by its corresponding proton Larmor frequency.
Neglecting $O(\varepsilon^2)$ terms:

$$\rho \approx \begin{pmatrix} \frac{1}{4} + \frac{\varepsilon}{2} & \frac{1}{4} \\ \\
\frac{1}{4} & \frac{1}{4} - \frac{\varepsilon}{2} \end{pmatrix} = \frac{1}{4} \mathbb{I} + \frac{\varepsilon}{2} I_z \otimes \mathbb{I} + \frac{\varepsilon}{2} \mathbb{I} \otimes I_z = \frac{1}{4} \mathbb{I} + \frac{\varepsilon}{2} I_z^{(1)} + \frac{\varepsilon}{2} I_z^{(2)}. \quad (1.47)$$

Note that given a density matrix $\rho$, the polarization of the $i$th spin is:

$$\varepsilon_i = 2\text{tr} \left( \rho I_z^{(i)} \right). \quad (1.48)$$

This polarization bias is actually obtained here by tracing out all other spins, and obtaining a density matrix of the form of Eq. 1.45 for the remaining spin.

The gyromagnetic ratio ($\gamma$) of protons is roughly 4 times higher than the gyromagnetic ratio of $^{13}$C, and so is the ratio between their equilibrium polarizations. For instance in $^{13}$C-chloroform, the density matrix of the proton and $^{13}$C is:

$$\rho = \begin{pmatrix} \frac{1+4\varepsilon}{4} & \frac{1-4\varepsilon}{4} \\ \\
\frac{1-4\varepsilon}{4} & \frac{1+4\varepsilon}{4} \end{pmatrix} = \frac{3}{4} + \frac{\varepsilon}{4} \text{diag}(5, -3, 3, -5) + O(\varepsilon^2). \quad (1.49)$$

In our spin system, $^{13}$C$_2$-trichloroethylene (TCE, see Figure 1.1), consisting of a proton and two $^{13}$C, the equilibrium density matrix is

$$\rho = \begin{pmatrix} \frac{1+\varepsilon}{2} & \frac{1-\varepsilon}{2} \\ \\
\frac{1-\varepsilon}{2} & \frac{1+\varepsilon}{2} \end{pmatrix} \otimes \begin{pmatrix} \frac{1+4\varepsilon}{4} & \frac{1-4\varepsilon}{4} \\ \\
\frac{1-4\varepsilon}{4} & \frac{1+4\varepsilon}{4} \end{pmatrix} = \frac{3}{8} \text{diag} \left( 6, -2, 4, -4, 4, -4, 2, -6 \right) + O(\varepsilon^2), \quad (1.50)$$

where C1 is the MSB, C2 is the middle spin, and H is the LSB.

![Figure 1.1: $^{13}$C$_2$-Trichloroethylene, our 3-spin system comprising of a proton (H), and two labeled carbons, C1 and C2. The three chlorine atoms (green) have 3/2 spin nuclei and a negligible coupling to the rest of the spin system. The coupling only broadens the spectral lines of the carbons, and therefore the chlorines are ignored throughout this work.](image)

1.2.4 Thermalization and Dephasing

The net magnetization of an ensemble of spins, once disturbed, returns to thermal equilibrium by two dissipation processes [45]. The longitudinal magnetization, i.e., the magnetization parallel to the magnetic field relaxes by a process often called $T_1$ relaxation, thermalization, or longitudinal relaxation, with $T_1$ time constant:

$$M_z(t) = (M_z(0) - M_{z,eq}) e^{-\frac{t}{T_1}} + M_{z,eq}. \quad (1.51)$$

Here $M_z$ is the longitudinal magnetization (proportional to $\langle I_z \rangle$ and to the polarization), and $M_{z,eq}$ is the longitudinal magnetization at thermal equilibrium. $T_1$ is calculated by inverting the spin’s polarization
using a 180° pulse, measuring the spin’s polarization recovery and fitting the results to the exponential model.

The transversal magnetization, which is perpendicular to the magnetic field, precesses around the z axis. Local magnetic field fluctuations (that act as a dephasing channel) cause the spins to precess at different angular frequency, thus decaying the net transversal magnetization in a process called transverse relaxation, decoherence, or dephasing, with $T_2$ time constant:

$$M_\perp(t) = M_\perp(0)e^{-\frac{t}{T_2}}. \quad (1.52)$$

Here $M_\perp$ is the size of the transversal magnetization, proportional to $\sqrt{(I_x)^2 + (I_y)^2}$. Practically, the principle magnetic field is not uniform throughout the sample, therefore even when excluding the temporal fluctuations, the variance of the spins’ precession increases, and the transversal magnetization decays faster - by an effective time constant marked $T_2^*$. In the spectrum, $T_2^*$ equals $\frac{1}{\Delta \nu}$, where $\Delta \nu$ is the width of the spin’s peakwidth at half-height. $T_2$ can be measured using spin echo techniques [13], which cancel out the non-uniformity of the magnetic field.

### 1.2.5 Product Operator Formalism

In NMR, density matrices are often decomposed into a sum of product operators [71]. For a single qubit, the Bloch sphere representation (section 1.1.4) is the decomposition of $\rho$ to the set $O = \left\{ \frac{1}{\sqrt{2}}, \frac{\sigma_x}{\sqrt{2}}, \frac{\sigma_y}{\sqrt{2}}, \frac{\sigma_z}{\sqrt{2}} \right\}$. For n qubits, the product operator set is $O \otimes^n$, which constitutes an orthonormal basis of matrices under the Hilbert-Schmidt (HS) inner product:

$$\forall \Gamma_i, \Gamma_j \in O \otimes^n, \quad \langle \Gamma_i, \Gamma_j \rangle = \text{tr} \left( \Gamma_i^\dagger \Gamma_j \right) = \text{tr} \left( \Gamma_i \Gamma_j \right) = \delta_{i,j}. \quad (1.53)$$

For two qubits, the set $O \otimes^2 = \left\{ \frac{1}{2}, \frac{1}{2} \sigma_x, \frac{1}{2} \sigma_y, \frac{1}{2} \sigma_z | \forall j, k \in \{x, y, z\} \right\}$ spans the 4 x 4 matrix space. For example:

$$|00\rangle \langle 00| = |0\rangle \langle 0| \otimes |0\rangle \langle 0| = \left( \frac{I_2 + \sigma_z}{2} \right) \otimes \left( \frac{I_4 + \sigma_z \otimes \sigma_z + \sigma_x \otimes \sigma_y + \sigma_y \otimes \sigma_x}{4} \right) = \frac{1}{4} \left( I_4 + \sigma_z \otimes \sigma_x \right) \quad (1.54)$$

$$\frac{1}{2} |00\rangle \langle 00| + \frac{1}{2} |11\rangle \langle 11| = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \frac{1}{4} \left( I_4 + \sigma_z \otimes \sigma_x \right) \quad (1.55)$$

$$\frac{|01\rangle - |10\rangle}{\sqrt{2}} \otimes \frac{|01\rangle - |10\rangle}{\sqrt{2}} = \frac{1}{2} \begin{pmatrix} 0 & 1 & -1 & 1 \\ 1 & 0 & -1 & 1 \\ -1 & -1 & 0 & 0 \\ 1 & 1 & 0 & 0 \end{pmatrix} = \frac{1}{4} \left( I - \sigma_x \otimes \sigma_x - \sigma_y \otimes \sigma_y - \sigma_z \otimes \sigma_z \right). \quad (1.56)$$

The thermal equilibrium state of TCE (equation 1.50) can also be expressed using product operators:

$$\rho = \frac{I_4}{8} + \frac{\varepsilon}{8} \left( \sigma_z \otimes I_4 + \sigma_x \otimes \sigma_z \otimes I_2 + 4I_4 \otimes \sigma_z \right). \quad (1.57)$$

A general linear combination of product operators constitutes a legitimate density matrix if it is
Hermitian, positive-semidefinite and has a trace of 1. Any real linear combination of product operators in $O^{\otimes n}$ is hermitian; the trace is equal to the coefficient of the $I/4$ element, as the rest of the operators are traceless. However, determining if a sum of product operators is positive-semidefinite is hard even for $O(n)$ terms of the sum. Representing a given density matrix to its product operator form is done by projecting it on the different product operators, in a similar way to finding the coordinate of a vector in a given basis:\footnote{Interestingly, since the product operators are hermitian, the projection under HS inner product of a density matrix $\rho$ on an operator $\Gamma$ equals the expectation value of the observable $\Gamma$ for $\rho$. In this interpretation, the product operators’ coefficients define the expectation values of various independent observables.}

$$\rho = \sum_i (\Gamma_i, \rho) \cdot \Gamma_i = \sum_i \text{tr}(\Gamma_i^\dagger \rho) \cdot \Gamma_i.$$  \hspace{1cm} (1.58)

For product operators which are not normalized:

$$\rho = \sum_i \frac{(\Gamma_i, \rho)}{\langle \Gamma_i, \Gamma_i \rangle} \cdot \Gamma_i = \sum_i \frac{\text{tr}(\Gamma_i^\dagger \rho)}{\text{tr}(\Gamma_i^\dagger \Gamma_i)} \cdot \Gamma_i.$$  \hspace{1cm} (1.59)

Hereinafter we will refer only to the traceless part of the density matrix (often called the deviation density matrix), since the identity matrix is unaffected by the Hamiltonian.

Unitary operations can be represented by an exponent of product operators. A unitary operation on a single qubit is a rotation on the Bloch sphere. We denote the unitary propagator of a rotation by an angle $\phi$ around a direction $\hat{r}$ by $[\phi]_{\hat{r}}$. In NMR it is conventional not to directly use Pauli matrices but spin $1/2$ operators denoted $\vec{I}$ or $\vec{S}$ which are defined as $\frac{1}{2} \vec{\sigma}$. Using the Taylor expansion of the exponent, we can reach the following expression for the rotation operator:

$$[\phi]_{\hat{r}} = e^{-i \phi \vec{I} \cdot \hat{r}} = e^{\frac{-i}{4} \phi (\vec{\sigma} \cdot \hat{r})} = e^{\frac{1}{2} \phi} = e^{i \phi} \cos \left( \frac{\phi}{2} \right) - i \hat{r} \cdot \vec{\sigma} \sin \left( \frac{\phi}{2} \right).$$  \hspace{1cm} (1.60)

For example, a $90^\circ$ rotation around $\hat{y}$ applied to $|0\rangle$ is calculated as

$$\left| 0 \right\rangle \left\langle 0 \right| \rightarrow e^{-i \frac{\pi}{4} \vec{\sigma} \cdot \hat{y}} \left| 0 \right\rangle \left\langle 0 \right| e^{i \frac{\pi}{4} \vec{\sigma} \cdot \hat{y}} = \frac{1}{\sqrt{2}} \begin{pmatrix} \frac{1}{2} - i \sigma_y & 2 + i \sigma_y \\ 2 - i \sigma_y & \frac{1}{2} \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 & i \sigma_y \\ -i \sigma_y & 1 \end{pmatrix} = |+\rangle \langle + |.$$  \hspace{1cm} (1.61)

Similarly, the evolution of a system under heteronuclear J-coupling is

$$[\phi]_{1,S} = e^{-i \phi \vec{I} \cdot \hat{r}} = e^{-i \frac{\pi}{4} \vec{\sigma} \cdot \hat{y}} = \begin{pmatrix} e^{i \frac{\pi}{4}} & e^{i \frac{\pi}{4}} \\ e^{-i \frac{\pi}{4}} & e^{-i \frac{\pi}{4}} \end{pmatrix} = \cos \left( \frac{\phi}{4} \right) \vec{1}_2 - i \sin \left( \frac{\phi}{4} \right) \vec{\sigma}_z \otimes \vec{\sigma}_z.$$  \hspace{1cm} (1.62)

When applied to $\vec{\sigma}_x \otimes \vec{1}_2$, the transformation is a rotation on a plane on the matrix space, which consists of $\vec{\sigma}_z \otimes \vec{1}_2$ and $\vec{\sigma}_y \otimes \vec{\sigma}_z$. 


$\sigma_x \otimes \mathbb{I}_2 \xrightarrow{\sigma^t,\sigma} \left[ \cos \left( \frac{\phi}{4} \right) \mathbb{I}_4 - i \sin \left( \frac{\phi}{4} \right) \sigma_z \otimes \sigma_z \right] \left( \sigma_x \otimes \mathbb{I}_2 \right) \left[ \cos \left( \frac{\phi}{4} \right) \mathbb{I}_4 + i \sin \left( \frac{\phi}{4} \right) \sigma_z \otimes \sigma_z \right]$

\[= \left[ \cos \left( \frac{\phi}{4} \right) \sigma_x \otimes \mathbb{I}_2 + \sin \left( \frac{\phi}{4} \right) \sigma_y \otimes \sigma_y \right] \left[ \cos \left( \frac{\phi}{4} \right) \mathbb{I}_4 + i \sin \left( \frac{\phi}{4} \right) \sigma_z \otimes \sigma_z \right] \tag{1.63}\]

\[= \cos \left( \frac{\phi}{2} \right) \sigma_x \otimes \mathbb{I}_2 + \sin \left( \frac{\phi}{2} \right) \sigma_y \otimes \sigma_y.\]

### 1.3 NMR Quantum Computing (NMRQC)

In NMR, quantum computation is performed on a sample, either liquid or solid, placed in a constant magnetic field [15,19,64]. Each molecule in the sample is a quantum register in which the spin 1/2 nuclei (hereinafter spins) are the qubits. The qubit is in the state $|0\rangle$, when aligned with the magnetic field and in the state $|1\rangle$ when aligned against the magnetic field. In solution, the molecules rapid isotropic tumbling averages out the inter molecule interactions, effectively isolating them from one another. Each molecule ideally receiving the same control, i.e., the RF field amplitude is homogeneous throughout the sample. Because of the macroscopic number of molecules, the output is a detectable electromagnetic signal – the sum of signals from all the molecules (i.e., the net magnetization).

In NMRQC, single qubit quantum gates can be implemented by free precession combined with transmitting RF fields on the sample at a frequency close to the resonance frequency of the spin. For example, a pulse rotating the spin orientation by $180^\circ$ around the x axis is a NOT gate. Interactions between spins (e.g., J-coupling) are utilized to perform two qubit operations, which complete a set of universal gates [19]. These interactions can’t be turned off, hence keeping spins unchanged is not trivial, and require various techniques such as spin echo [36].

#### 1.3.1 Pseudo Pure States and the Scalability Problem

Most quantum algorithms require qubits in a pure state, unlike the highly mixed state of spins in NMR at thermal equilibrium. The Pseudo-pure state (PPS) was introduced [18,31] to allow quantum computation in this scenario:

$$\rho_{\text{res}} = \frac{1}{2^n} \mathbb{I}_{2^n} + p|\psi\rangle\langle\psi| \tag{1.64}$$

where $n$ is the number of the qubits. Applying a unitary matrix $U$ to the pseudo pure state is similar to applying it to $|\psi\rangle\langle\psi|$:

$$U \rho_{\text{res}} U^\dagger = U \left( \frac{1}{2^n} \mathbb{I}_{2^n} + p|\psi\rangle\langle\psi| \right) U^\dagger = \frac{1}{2^n} \mathbb{I}_{2^n} + pU|\psi\rangle\langle\psi|U^\dagger. \tag{1.65}$$

The NMR signal received from a PPS is proportional to the signal received from the equivalent pure state (p the ratio between the signals), thus making quantum computation in NMR possible. However, when generating a PPS from a system of $n$ spins, $p$ decreases exponentially with $n$, a problem known as the scaling problem of NMRQC (see section 4.1.1 in [77]). Algorithmic cooling, introduced in the next section, was designed originally as a tool that may solve the scaling problem in the far future.

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1.3.2 Previous Experimental Work on NMRQC

The transition from theory to practice in NMRQC has been quick as NMR was already a mature technology. Cory Fahmi and Havel [17], implemented a universal set of quantum gates on two and three spin systems in liquid state NMR, demonstrated entanglement and superposition, and generated PPS using gradient-pulse techniques\(^5\).

One of the first NMRQC algorithm implemented [15] was Grover’s search algorithm [32] on \(^{13}\text{C}-\)chloroform, a two spin system. The system was prepared in a PPS equivalent to the state \(|00\rangle\) by temporal averaging. A Walsh-Hadamard transform was applied on the system, followed by a single Grover iterator. The final state of the system was obtained using quantum state tomography\(^6\). Other important works include quantum state teleportation [54] implemented on TCE and a factoring of 15 [74], which was implemented on a custom-synthesized molecule containing 7 spin half nuclei. For additional algorithms implemented in NMR, refer to [35].

The largest NMR quantum computer universally controlled to date is \(^{13}\text{C}&^{15}\text{N}\) labeled l-histidine [52]. 11 qubits and one qutrit were fully controlled in this 14 half spin molecule. On a different experiment [69], a 13 qubits cat state \(|0\rangle^{13} \otimes |0\rangle^{13} + |1\rangle^{13} \rangle\) was created on tetramethylsilane (TMS).

1.4 Overview of Algorithmic Cooling

1.4.1 Polarization Enhancement

The holy grail of NMR is to magnify the polarization of spins, as it increases the signal detected by the probe. In addition, qubits in pure state are required for NMRQC, as the PPS solution is not scalable. The polarization of the spins can be improved directly by either increasing the magnetic field, or by reducing the temperature. Both methods are expensive; cooling the sample is not always possible as it may change the characteristics of the material. Signal to noise enhancement by repetitions of the experiment is often utilized in NMR as well as in magnetic resonance imaging (MRI). However, the improvement is proportional to the square root of the repetitions number and limited by the thermalization times of the system, hence time consuming. Effective cooling is a different approach, cooling the spin system degrees of freedom, without cooling the sample [51,67,72]. Spin cooling methods which are not discussed in this work are dynamic nuclear polarization [4], para-hydrogen in two spin systems [3], and hyperpolarized xenon [56].

1.4.2 Reversible Polarization Compression (RPC)

The entropy of the spin system can be manipulated using quantum logic gates, effectively cooling some spins while heating others. For example, given a spin system with two heteronuclear spins I and S, with gyromagnetic ratios \(\gamma_I\) and \(\gamma_S\) s.t. \(\gamma_I > \gamma_S\). In thermal equilibrium \(\varepsilon_{I,eq} > \varepsilon_{S,eq}\), hence applying a SWAP gate on the two spins will increase the polarization of spin S, effectively cooling it while heating spin I [10]. In \(^{13}\text{C}-\)Chloroform, as mentioned earlier, the proton’s gyromagnetic ratio (and therefore its equilibrium polarization) is roughly 4 times higher than \(^{13}\text{C}\). Applying an in-place swap on the two spins, i.e., CNOT(C,H) \(\rightarrow\) CNOT(H,C) \(\rightarrow\) CNOT(C,H), results in a polarization swap - the carbon is 4 times cooler than its equilibrium polarization, and the hydrogen is 4 times hotter. Alternatively, applying a refocused INEPT\(^7\) pulse [51], which is equivalent to CNOT(C,H) \(\rightarrow\) CNOT(H,C), results in cooling the

\(^5\)Not to be confused with gradient ascent methods described later.
\(^6\)Appendix B.2 shows how elements of the density matrix are extracted from the spectrum.
\(^7\)INEPT - Insensitive Nuclei Enhanced by Polarization Transfer.
carbon by a factor of 4, while leaving the hydrogen with zero polarization; although its state is correlated with the carbon, if the carbon is traced out, H remains in a completely mixed state.

In a different approach, in-place lossless data compression techniques applied on bit strings, reduce the number of bits required to represent each string on average [20]. Practically some bits become more random while others become less random or even constant thus redundant. In analogy, the spin ensemble is a large number of strings, therefore data compression techniques can reduce the randomness (i.e., increase the polarization) of some spins while increasing the randomness of other spins [67,72].

For example, given a spin system of three homonuclear spins at equilibrium, each with \(\varepsilon\) equilibrium polarization, the transformation \(|011\rangle \leftrightarrow |100\rangle\) called 3-bit compression (3BC) increases the polarization of the left spin:

\[
\rho_i = \begin{pmatrix}
\frac{3\varepsilon}{8} & \varepsilon & -\varepsilon \\
\varepsilon & \frac{\varepsilon}{2} & -\varepsilon \\
-\varepsilon & -\varepsilon & -3\varepsilon \\
\end{pmatrix}
\]

\[
\rightarrow \rho_f = \begin{pmatrix}
\frac{3\varepsilon}{8} & \varepsilon & -\varepsilon \\
\varepsilon & \frac{\varepsilon}{2} & -\varepsilon \\
-\varepsilon & -\varepsilon & -3\varepsilon \\
\end{pmatrix}
\]

It is convenient to write the density matrices in a shifted and scaled form:

\[
\rho'_i = \text{diag} (3, 1, 1, -1, 1, -1, -1, -3) \rightarrow \rho'_f = \text{diag} (3, 1, 1, 1, -1, -1, -1, -3).
\]

Following 3BC, the polarization of the left spin is enhanced by a factor of \(\frac{3}{2}\)

\[
\sum_{i,j=0,1} \langle 0ij | \rho_f | 0ij \rangle - \langle 1ij | \rho_f | 1ij \rangle = \frac{3}{2} \varepsilon
\]

while the polarizations of the other two spins are \(\frac{1}{2} \varepsilon\). Note that the final density matrix can’t be written as a tensor product, as spins are now correlated (the total IC is larger than the sum of the spins’ independent IC). To show that, see the difference between \(\rho'_f\) and the following shifted and scaled density matrix with polarizations \(\frac{3\varepsilon}{2}, \frac{1\varepsilon}{2}, \frac{1\varepsilon}{2}\) and no correlations:

\[
\rho'_f = \text{diag} \left( \frac{3}{2}, \frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2} \right)
\]

The initial and final density matrices can be expressed in the product operators form by utilizing equation 1.59:

\[
\frac{\text{tr} (\rho_i I_z^{(1)})}{\text{tr} (I_z^{(1)} I_z^{(1)})} = \frac{\varepsilon}{4} \quad \frac{\text{tr} (\rho_i I_z^{(2)})}{\text{tr} (I_z^{(2)} I_z^{(2)})} = \frac{\varepsilon}{4} \quad \frac{\text{tr} (\rho_i I_z^{(3)})}{\text{tr} (I_z^{(3)} I_z^{(3)})} = \frac{\varepsilon}{4}
\]

\[
\frac{3\varepsilon}{8} \quad \frac{\varepsilon}{8} \quad \frac{\varepsilon}{8} \quad \frac{\varepsilon}{8} \quad \frac{\varepsilon}{8}
\]

\[
\frac{\text{tr} (\rho_f I_z^{(1)})}{\text{tr} (I_z^{(1)} I_z^{(1)})} = \frac{3\varepsilon}{8} \quad \frac{\text{tr} (\rho_f I_z^{(2)})}{\text{tr} (I_z^{(2)} I_z^{(2)})} = \frac{\varepsilon}{8} \quad \frac{\text{tr} (\rho_f I_z^{(3)})}{\text{tr} (I_z^{(3)} I_z^{(3)})} = \frac{\varepsilon}{8}
\]

\[
\frac{\text{tr} (\rho_f I_z^{(1)} I_z^{(2)} I_z^{(3)})}{\text{tr} (I_z^{(1)} I_z^{(2)} I_z^{(3)})} = \frac{\varepsilon}{2}
\]
Hence,

$$\rho_i = \frac{1}{8} + \frac{\varepsilon}{4} \left( f_z^{(1)} + f_z^{(2)} + f_z^{(3)} \right)$$

$$\rho_f = \frac{1}{8} + \frac{\varepsilon}{4} \left( \frac{3}{2} f_z^{(1)} + \frac{1}{2} f_z^{(2)} + \frac{1}{2} f_z^{(3)} + 2 f_z^{(1)} f_z^{(2)} f_z^{(3)} \right).$$

(1.72)

Note that the polarization of the first spin is invariant to any permutation of the top four diagonal entries, as well as any permutation of the bottom four diagonal entries. Therefore other compression pulses may maximize the polarization of the left spin, while generating different correlations.

### 1.4.3 Bounds on Polarization Enhancements by RPC

Upper bounds on polarization enhancement can be derived by interpreting the spin state in terms of information theory. In the pioneering work by Shannon [20], the information content (IC) and entropy ($H$) of random variables such as the spin state were defined. The relation between a single spin’s polarization and IC for $\varepsilon \ll 1$ is given by the following equation [24].

$$H_{1\text{qubit}} = \frac{1 - \varepsilon}{2} \ln \left( \frac{1 - \varepsilon}{2} \right) + \frac{1 + \varepsilon}{2} \ln \left( \frac{1 + \varepsilon}{2} \right) = 1 - \frac{\varepsilon^2}{\ln 4} + O(\varepsilon^4)$$

$$IC_{1\text{qubit}} = 1 - H = \frac{\varepsilon^2}{\ln 4} + O(\varepsilon^4).$$

(1.73)

The information content of a spin system is invariant to reversible operations and therefore bounds the maximal IC a single spin can reach by utilizing lossless manipulations such as quantum gates. This bound, called Shannon’s bound, limits the maximal polarization of a single spin, given an initial state of the spin system.

For example, in TCE, the IC of the proton and the two carbons at thermal equilibrium is:

$$IC_{eq} = \frac{\varepsilon^2_{H,eq}}{\ln 4} + \frac{\varepsilon^2_{C,eq}}{\ln 4} = \left[ \frac{\gamma H}{\gamma C} + 2 \right] \frac{\varepsilon^2_{C,eq}}{\ln 4} \approx 18 \frac{\varepsilon^2_{C,eq}}{\ln 4}. $$

(1.74)

Shannon’s bound is reached when a single spin holds all the equilibrium information content, hence keeping the other spins infinitely hot, holding no IC:

$$IC_{eq} \approx 18 \frac{\varepsilon^2_{C,eq}}{\ln 4} = \frac{\varepsilon_{max}^2}{\ln 4}$$

$$\varepsilon_{max} \approx \sqrt{18} \varepsilon_{C,eq} = 4.24 \varepsilon_{C,eq}. $$

(1.75)

Similarly, given a system of $n$ spins with equal polarization $\varepsilon$, the maximal polarization of a single spin obtainable using RPC is bounded by $\sqrt{n} \varepsilon$, as long as the final polarization is much smaller than 1. Note that although we focus on the IC of each spin separately, as it relates directly to the polarization, the correlations may also contain IC. For example, in a system of two qubits with equal probability to be in the states $|00\rangle$ and $|11\rangle$, each spin, individually, is at a completely mixed state (IC=0). However the system is not in a completely mixed state, thus the IC of the system is not 0 (it is in fact 1). Hence the correlation between the spins contain the missing IC.

Shannon’s bound is not necessarily reachable in spin systems, as their evolution is limited to unitary
propagators. A tight bound on the dynamics of a spin system was given by Sørensen [72], stating that the maximal polarization of the leftmost spin is achieved by diagonalizing the density matrix and ordering the eigenvalues in a decreasing order. Note that the method can be achieved by unitary operations and that the polarization of the leftmost spin is the difference between the sum of the top diagonal and the bottom diagonal of the density matrix. In three homonuclear spin, the spin dynamics bound for the cooling factor is 1.5, as reached by 3BC. According to Shannon’s bound, the cooling factor is limited to $\sqrt{3} \approx 1.73$, yet this factor not achievable by in-place compression.

### 1.4.4 Algorithmic Cooling

Algorithmic cooling of spins (AC) [9, 28, 66] counter intuitively utilizes the heat bath, that decays polarizations to thermal equilibrium, to cool spins beyond Shannon’s bound. AC requires a spin system where some spins, called reset spins, thermalize (or otherwise regain thermal equilibrium polarization) significantly faster than other spins, named computation spins. Reversible entropy manipulation (e.g., compression, swap) is applied to the spin system, transferring some of the computation spins’ entropy to the reset spins, which ideally lose the excess entropy to the environment, and thus cooling the spin system beyond Shannon’s bound. The process is similar to a heat engine [2, 11, 33, 46, 60, 76] and can be repeated, further cooling the system, until it converges to a stable trajectory (limit-cycle) in the density-matrix space. Practically, the computation spins also lose some of their polarization when the reset spins thermalize, hence the efficiency of AC is limited by the $T_1$ ratio between the computation spins and the reset spins.

Various cooling algorithms emerged from this principle. We start by algorithms assuming the $T_1$ of the reset spins is vastly shorter than the $T_1$ of the computation spins, the equilibrium polarization of all the spins is the same ($c$) and the final polarizations are much smaller than 1.

The first cooling algorithm introduced in [9], relies on the law of large numbers and is not applicable on small molecules. A more experimentally feasible and easier to analyze class of algorithms is named practicable algorithmic cooling (PAC) [28], which relies on 3BC, polarization transfer (PT) and reset steps. The PAC2 algorithm utilizes $2J$ computation spins and a single reset spin to ideally cool one of the computation spins by a factor of $\left(\frac{2}{3}\right)^J$. For instance, a single spin in a three-spin system can be cooled by a factor of 1.5; in a five-spin system, a single spin can be cooled by a factor of 2.25.

PAC2 is not the ultimate cooling of three spins. For instance, adding a reset step and another 3BC can cool the system further. The Fernandez algorithm [27], improves the 3BC building block by multiple repetitions of the following steps:

1. Apply 3BC on the three spins A, B, C, cooling spin C
2. Let the reset spins A and B thermalize to their equilibrium polarization, while C retain its polarization

After a single round, spin C is cooled by a factor of 1.5 (as was shown in section 1.4.2), and asymptotically the algorithm reaches a cooling factor of 2. If A is the only reset spin in the spin system, step 2 can be replaced by a reset, PT(A → B) and another reset.

By recursively applying an exhaustive procedure on more spins, we get the Fibonacci algorithm [66]. Additional exhaustive algorithms are the tri-bonacci, the k-bonacci, and the all-bonacci. Semi-optimal algorithms [26] such as mPAC and mFib, bridge between the exhaustive algorithms and the practicable AC by limiting the number of repetitions in each recursive level. For instance, by applying the mPAC algorithm on $2J$ computation spins and a single reset spin, a cooling factor of $(2 - 2^{-m})^J$ can be reached.
The partner pairing algorithm (PPA) \cite{65,66} utilizes a different approach and has proven to yield the highest possible polarization for any given number of reset steps. PPA consists of repeating the following steps:

1. Sort the diagonal of the density matrix in a descending order; \( a_{i,i} \geq a_{i+1,i+1} \forall i \)
2. Let the reset spin (the rightmost spin in the tensor product) thermalize to equilibrium

PPA is difficult to implement as each SORT step requires an exponential number of quantum gates. Another challenge is to sort the density matrix without keeping its diagonal entries in memory. Given \( n \) computation spins and one reset spin, PPA can cool a single computation spin by a factor of \( 2^{n-1} \).

Proton spins have roughly four times the equilibrium polarization of \(^{13}\)C, and often shorter \( T_1 \), which allows heat bath cooling - cooling without compression. As a particularly simple example, consider the \(^{13}\)C-chloroform example from section 1.4.2; this system can be trivially cooled beyond Shannon’s bound by applying a polarization transfer (PT) from the proton to the carbon, and waiting for the proton to regain some of its polarization (while the carbon is still cool). This sequence is called selective reset \cite{10}, and may be incorporated to AC schemes on heteronuclear molecules. In a three spin system such as \(^{13}\)C\(_2\)-TCE, a POTENT\(^8\) pulse sequence - which consists of applying selective resets on the two carbons, provides the first 3BC a better starting point than the equilibrium state (see table 1.1).

<table>
<thead>
<tr>
<th>POTENT Step</th>
<th>Polarization of C1,C2,H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium</td>
<td>( {1,1,4} )</td>
</tr>
<tr>
<td>SWAP(H,C1)</td>
<td>( {4,1,1} )</td>
</tr>
<tr>
<td>Reset H</td>
<td>( {4,1,4} )</td>
</tr>
<tr>
<td>SWAP(H,C2)</td>
<td>( {4,4,1} )</td>
</tr>
<tr>
<td>Reset H</td>
<td>( {4,4,4} )</td>
</tr>
</tbody>
</table>

Table 1.1: The polarization of the TCE spins during POTENT, assuming infinite \( T_1 \) ratios.

A possible application of AC and heat bath cooling outside the quantum information world is in clinical magnetic resonance spectroscopy (MRS); polarization enhancement translates to better signal to noise ratio, as recently demonstrated on amino acids \cite{25}.

### 1.4.5 Previous Experimental Work

In practice, the cooling factors reachable are greatly limited by the finite \( T_1 \) ratios (seldom better than 1 : 10 in liquid state). Dephasing, which reduces the efficiency of quantum gates, also reduces the reachable cooling. Cooling strictly by compression was done by Sørensen \cite{72} on methylenechloride. Chang, Vandersypen & Steffen \cite{14} applied compression on three fluorine \(^{19}\)F spins in \( C_2F_3Br \) to reach polarization enhancement of about 25%. Hereinafter polarization is expressed in units of carbon equilibrium polarization.

In TCE \cite{10}, a POTENT pulse sequence was applied and the final polarizations were 1.74 ± 0.01, 1.86 ± 0.01 and 3.77 ± 0.01 for C1, C2 and the proton respectively (see Figure 1.1), with IC=20.70 ± 0.06. Paramagnetic reagent was added to TCE, reducing the \( T_1 \) values of all the spins, but improving the thermalization time ratios \cite{29}. Given the \( T_1 \) values of the spins in that experiment \( 43 ± 4.0s, 20 ± 2.0s \)
and 3.5 ± 0.05s for C1, C2 and H respectively), and assuming the delay times actually used in the experiment, the cooling factors achievable using perfect pulses are 2.97, 2.60 and 3.73 for C1, C2 and the proton respectively. However these factors were not reached due to the inefficiency of the PT pulse sequences, mainly caused by off-resonance effects, dephasing, and imperfections in the pulse sequence. Applying a compression pulse on the spin system at the end of this experiment is futile, as C1 will be cooled by a factor of $\frac{1}{1.74+1.96+3.77} = 3.685$ at most$^9$, less than an ideal PT from H to C1.

The first full algorithmic cooling cycle was accomplished in solid state malonic acid [7], a 4-spin system (H as reset spin and three $^{13}$C). The single crystal sample with only 3% labelled molecules enabled a controlled spin diffusion which greatly reduced the repolarization time of the reset spin, reaching thermalization time ratios of $\approx 10,000$. The experiment was improved by utilizing GRAPE [42], an optimal control algorithm, to generate high fidelity pulses [63]. Four rounds of algorithmic cooling were applied on the three carbons, reaching maximal cooling factor of $5.58 \pm 0.07$, $2.77 \pm 0.07$ and $2.61 \pm 0.07$.

1.5 Goals of the Research and the Thesis Organization

The significant improvement in pulses efficiency by optimal control tools, which lead to multi round algorithmic cooling in solid state NMR [63], motivated us to attempt to improve the effective cooling performed on TCE [10] - to apply a full AC on liquid. While optimal control allows more efficient pulses, the $T_1$ ratios in liquid state NMR remain the main limitation on the achievable cooling. Cooling algorithms which consist of only two pulses were chosen due to the challenges of pulse generation. The two pulses are: a polarization exchange (PE) pulse, swapping the polarizations of H and C2, and a compression pulse, that cools C1.

We planned to cool C1 by implementing the following algorithm [23,24,27]:

1. Reset the proton (WAIT)
2. Polarization exchange (H$\leftrightarrow$C2)
3. Reset the proton (WAIT)
4. Compress on C1
5. Return to step #1 (until steady state)
6. Readout pulse
7. Acquisition

In each round (steps 1-4), the proton relaxes from the previous round, the polarization of the proton and C2 are swapped (by a polarization exchange pulse), and after the proton relaxes again, the round is concluded by applying a 3-bit compression to cool C1. Before the acquisition, another pulse is applied on the carbons to rotate their polarization to the xy-plane, making it visible in the spectrum (see the predicted state of the spin system throughout the algorithm in table 1.2). Note that we omitted the polarization transfer from C2 to C1, that concluded the first step of the POTENT pulse sequence used in the previous work [10], to reduce the number of pulses designed to two. The following table justifies this decision; in the proposed algorithm, the polarization of C1 and C2 (ideally) reach 4.5 and 4.0 respectively after the second SWAP step (between COMP #1 and COMP #2) - better than POTENT.

$^9$After 3BC, the polarization on the cooled spin is $\frac{1+1+3+3}{2}$. See proof at section 4.2.1
The rest of the thesis consists of the following chapters: Chapter 2 describes GRAPE, the optimal control algorithm and its implementation in the SIMPSON NMR simulation software. Chapter 3 describes the experimental apparatus and the process of pulse design and analysis. The various considerations of the cooling algorithm as a whole are described in chapter 4. Chapters 5 and 6 contain the results and the discussion respectively.
| Table 1.2: Predicted state of the system during AC, assuming perfect pulses, and infinite $T_1$ ratio between the computation spins and the reset spin. $\varepsilon_{C1}, \varepsilon_{C2}$ and $\varepsilon_H$ are the polarizations of C1, C2 and H respectively; $I_z^{C1} I_z^{C2} I_z^{H}$ column shows the coefficient of the trilinear correlation term of the density matrix. In this simulation we used 3BC as the compression step. |
Chapter 2

Numerical Tools in NMR

2.1 NMR Simulation with SIMSPON

SIMPSON [5] is an open source program that numerically simulates solid (and liquid) state NMR experiments\(^1\). The program is designed as a “computer spectrometer”, hence it uses native terms such as spin system, nuclear spin interactions, RF irradiation, acquisition etc. The user defines the experimental parameters and executes the simulation engine by a Tcl [1] scripting language file, allowing further usage flexibility. The simulation outputs the fid of the experiment (or the final density matrix) and also contains many useful procedures such as fast Fourier transform (FFT), phase correction and line broadening. Remark: the latter must be used as SIMPSON does not implement dephasing, and with no decay of the fid, the spectrum would have artificial sidebands.

2.1.1 The Input File

The input file to SIMPSON (see source code examples in appendix C) contains the following components:

1. **spinsys** - A structure that defines spin system parameters such as spin types, J-coupling constants, chemical shifts etc.

2. **par** - A structure that defines experimental parameters such as detection operator, sampling spectral width and spinning speed.

3. **pulseq** - A procedure that defines the pulse sequence.

4. **main** - The first procedure executed when the script starts. It calls the simulation engine **fsimpson** (potentially multiple times for parameter optimization), and may process the output spectrum and save the fid.

2.1.2 Typical Program Flow in Simulation Mode

1. **main** procedure is running until the command **fsimpson** is reached.

2. **fsimpson** calls the procedure **pulseq**.

\(^1\)SIMPSON was later extended to design pulses using optimal control, as discussed in section 2.4.
3. While `pulseq` is running, the program keeps track of the evolution of the density matrix during the pulse sequence, using the structures `spinsys` and `par`. The command `acq` is used for acquisition of a single data point, which will later be used for spectrum generation. Normally, `acq` will be used inside a loop, for a continuous acquisition of the data (i.e., the fid - free induction decay data) once the pulse sequence ends.

4. When `pulseq` ends, the control is returned to `main`.

5. Since no dephasing is simulated in SIMPSON, the fid data ends when there is still a signal, causing artifacts in the spectrum. Therefore, the fid is multiplied by a decaying exponent in order to avoid that (i.e., line broadening).

6. The fid and the spectrum are saved.

2.2 Optimal Control in NMR

Optimal control theory deals the problem of finding a way to control a system such that an optimality criterion is met, subject to constraints [8,12,44,58]. For example, a car is a system that can be approximated by a unit point mass with two state variables - its position and velocity. The car’s acceleration is defined by the gas and break pedals - the control variables. The optimality criterion can be the distance the car travels, and the constraint is the fuel consumption. Bellman developed a method to find optimal control by dynamic programming [8]. Pontryagin [58] used a variational approach.

In NMR, optimal control is used for designing and optimizing experiments for various applications such as imaging [16,48,61,79], liquid and solid state spectroscopy [37,38,42,43,59,73,75], quantum computation [40,41,68,80], dynamic nuclear polarization (DNP) [34,39,49,57] and algorithmic cooling in solid state [63].

2.3 GRAPE - GRadient Ascent Pulse Engineering

GRAPE [42] is an optimal control algorithm which designs shaped pulses contemplating to apply a state to state transformation, or a given unitary propagator. A pulse with random shape (i.e., random amplitudes and phases) is generated, and then monotonically improved by gradient ascent\(^2\) in respect to a target function. Robustness of the pulses to experimental parameters such as RF or primary magnetic field inhomogeneities is supported inherently by the algorithm. In this work we used the GRAPE implementation in SIMPSON [73]. Although GRAPE can integrate dissipation processes into the state to state optimization, they are not supported by SIMPSON.

2.3.1 State to State Algorithm

The GRAPE state-to-state algorithm finds the optimal amplitudes and phases of the RF fields that steer a given initial density matrix \(\rho(0) = \rho_0\), in a specified duration, \(T\), to a density matrix \(\rho(T)\) with maximum overlap with a desired target density matrix \(\rho_{\text{desired}}\). The Hilbert-Schmidt (HS) inner product of the initial and final density matrices was chosen\(^3\) as the target function to maximize:

\[
\Phi = \text{tr}\left\{\rho_{\text{desired}} \cdot \rho(T)\right\} = \text{tr}\left\{\rho_{\text{desired}} \cdot U \rho_0 U^{\dagger}\right\} \leq \text{tr}\left\{\rho_{\text{desired}}^2\right\}.
\]  

\(^2\)Not to be confused with a magnetic field gradient used in NMR experiments.

\(^3\)Note that this optimization assumes no dephasing occurs during the pulse duration. See the motivation to use HS inner product in appendix D.
Let $T$ be the RF pulse length, discretized in $N$ equal intervals of duration $\Delta t = T/N$. The pulse is assumed constant during each interval.

The evolution of the spin system during a time step $j$ is given by the propagator

$$U_j = \exp \left\{ -\frac{i \Delta t}{\hbar} (H_0 + H_{rf}) \right\}$$

(2.2)

where $k$ in the last expression goes over all combinations of channels (nucleus type) and axes (X/Y), $u_k(j)$ is the corresponding amplitude of that radio field, and $H_k$ is the RF Hamiltonian of the affected spins (refer to equations 1.36, 1.37 and 1.38). $\rho(T)$ can be expressed using $\rho_0$ and the time propagators:

$$\rho(T) = U_N U_{N-1} \cdots U_1 \rho_0 U_1^\dagger \cdots U_N^\dagger.$$  (2.3)

Substituting and rearranging:

$$\Phi = \text{tr} \left\{ \rho_{\text{desired}} \cdot U_N U_{N-1} \cdots U_1 \rho_0 U_1^\dagger \cdots U_N^\dagger \right\} =$$

$$= \text{tr} \left\{ U^\dagger_{j+1} \cdots U^\dagger_N \rho_{\text{desired}} \cdot U_N \cdots U_{j+1} U_j \cdots U_1 \rho_0 U_1^\dagger \cdots U_j^\dagger \right\}$$

$$= \text{tr} \{ \lambda_j \rho_j \}.$$  (2.4)

Where $\rho_j$ is the density operator $\rho(t = j\Delta t)$ and $\lambda_j$ is the desired density matrix, $\rho_{\text{desired}}$, backward propagated to the same time, $t$:

$$\rho_j = U_j \cdots U_1 \rho_0 U_1^\dagger \cdots U_j^\dagger$$

(2.5)

$$\lambda_j = U^\dagger_{j+1} \cdots U^\dagger_N \rho_{\text{desired}} \cdot U_N \cdots U_{j+1}.$$  (2.6)

Gradient ascent method finds a local maximum of a scalar target function by “walking” in the direction of its gradient. Since the system can evolve from one state to another in many paths, a local minima of the target function will often yield a pulse with satisfying efficiency. The expression for the derivatives of $\Phi$ by the control variables (i.e., the RF field amplitudes in the xy plane) is$^4$:

$$\frac{\delta \Phi}{\delta u_k(j)} = \frac{i \Delta t}{\hbar} \cdot \text{tr} (\lambda_j [\rho_j, H_k]).$$  (2.7)

Changing $u_k(j)$ in that direction will therefore increase $\Phi$. This forms the basis of the GRAPE algorithm:

1. Guess initial controls $u_k(j)$\forall j, k .

2. Starting from $\rho_0$ calculate $\rho_j = U_j \cdots U_1 \rho_0 U_1^\dagger \cdots U_j^\dagger$ for all $j \leq N$.

3. Starting from $\lambda_N$, calculate $\lambda_j$ for all $j \leq N$.

$^4$See proof at appendix E.
4. Add $\eta \frac{\delta \Phi}{\delta u_k(j)}$ to the amplitudes $u_k(j)$.

5. Return to step 2.

Figures 2.1 and 2.2 show two simple examples of the pulse evolution from the initial guess to the final optimal pulse. The somewhat stochastic modulation of the pulse implies high bandwidth even for selective pulses, hence it is advised not to use the terms “soft” or “hard” pulse for shaped pulses.

Figure 2.1: An optimization of a pulse that rotates the hydrogen spin from z to x in 1.5 msec in TCE. The pulse is made of 500 points, and due to the simplicity and lack of any constraint it converged after only 12 iterations. The initial guess pulse is in blue, intermediate pulses are in gray and the final pulse is in red. Only the amplitude of the pulse is displayed.
Figure 2.2: Iterations of a simple pulse optimization. The 1 msec pulse rotates the hydrogen spin in TCE from $z$ to $x$. The pulse is made of 1000 points, separated by 1 $\mu$sec, and due to the simplicity and lack of any constraint it converged after only 8 iterations. The top graph shows the X (blue) and Y (green) amplitudes of the initial (random) pulse, and the sequent graphs are the pulses generated by the next iterations of the algorithm.
2.3.2 Degrees of Freedom of the Unitary Transformation Applied by the Pulse

The pulse generated by GRAPE in state to state mode, has more freedom than a pulse that is designed to reach a good approximation of a specific unitary transformation. Intuitively, the freedom arises from the fact that a unitary operation defines the transformation of all states, while state-to-state mode defines the transformation of only part of the states. We chose this mode since the freedom allows a generation of much shorter pulses, therefore increasing their efficiency, as the dephasing during the pulse is reduced. However this freedom may cause an undesired transformation when applying the pulse on density matrices different than $\rho_0$. For example, the following state to state transformation seems to imply SWAP(2,3) gate:

$$I_z(1) + I_z(2) + 4I_z(3) \rightarrow I_z(1) + 4I_z(2) + I_z(3). \quad (2.8)$$

Or in shifted and scaled form:

$$\rho'_0 = \text{diag}(6, -2, 4, -4, 2, -6)$$

$$\rho'_{\text{desired}} = \text{diag}(4, 6, -2, -4, 2, -4, 6). \quad (2.9)$$

However, since there are two spins with the same polarization both in the initial density matrix and in the final density matrix, a pulse satisfying the transformation in equation 2.8, may apply SWAP(1,2) followed by SWAP (2,3). When applied on a different density matrix, clearly this pulse will not apply SWAP(2,3) gate:

$$4I_z(1) + I_z(2) + 2I_z(3) \rightarrow I_z(1) + 2I_z(2) + 4I_z(3). \quad (2.10)$$

We begin the analysis by writing $\rho_0$ and $\rho_{\text{desired}}$ in the following representation:

$$\rho_0 = \sum_i \lambda_i |\psi_i\rangle \langle \psi_i|$$

$$\rho_{\text{desired}} = \sum_i \lambda_i |\phi_i\rangle \langle \phi_i|. \quad (2.11)$$

Here, $\lambda_i$ are the (common) eigenvalues, $|\psi_i\rangle$ and $|\phi_i\rangle$ are the eigenvectors of $\rho_0$ and $\rho_{\text{desired}}$ respectively. The algorithm maximizes $\text{tr}(U \rho_0 U^\dagger \rho_{\text{desired}})$. In appendix D, we show that for every $U$,

$$\text{tr}(U \rho_0 U^\dagger \rho_{\text{desired}}) \leq \text{tr}(\rho_{\text{desired}} \rho_{\text{desired}}) = \sum_i \lambda_i^2. \quad (2.13)$$

Hence maximizing the trace is done by transforming each eigenvector of $\rho_0$ to an eigenvector in $\rho_{\text{desired}}$ that has the same eigenvalue. In case of no degeneracy (i.e., $\lambda_i \neq \lambda_j$ for every $i, j$), the $U$ that maximizes the trace has to transform each $|\psi_i\rangle$ to $|\phi_i\rangle$ but has the freedom of choosing the phases:

$$U = \sum_i e^{i\theta_i} |\phi_i\rangle \langle \psi_i| \quad (2.14)$$

For example, rotating a spin from the $z$ to the $x$ axis, can be done in many ways. Choosing $\theta_1 = \theta_2$ yields a Hadamard gate (see Figure 2.3)

---

5 An $n \times n$ matrix has only $n-1$ free parameters (phases) as the global phase has no physical meaning.
Choosing opposite phases yields a $\frac{\pi}{2}$ rotation around the $y$ axis.

$$U = |+\rangle \langle 0| - |-\rangle \langle 1| = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} = e^{\frac{\pi i}{2} I_y}.$$  \hspace{1cm} (2.16)$$

In case of degeneracy, an eigenvector of $\rho$ can be mapped to any combination of eigenvectors of $\rho_{\text{desired}}$ that share its eigenvalue, keeping the trace maximized. Formally, Let $P_0^{(i)}$ be the set of eigenvectors of $\rho_0$ sharing a eigenvalue $\lambda_i$, and let $P_{\text{desired}}^{(i)}$ be the set of the corresponding eigenvectors of $\rho_{\text{desired}}$. Any unitary transformation that transforms the subspace spanned by $P_0^{(i)}$ to the subspace spanned by $P_{\text{desired}}^{(i)}$, for every $i$, will maximize the trace.

$$\text{tr}(U \rho_0 U^\dagger \rho_{\text{desired}}) = \sum_i \sum_{v \in P_{\text{desired}}^{(i)}} \langle v | U \rho_0 U^\dagger \rho_{\text{desired}} | v \rangle =$$

$$= \sum_i \sum_{v \in P_{\text{desired}}^{(i)}} \lambda_i \langle v | U \rho_0 U^\dagger | v \rangle = \sum_i \sum_{w \in P_0^{(i)}} \lambda_i \langle w | \rho_0 | w \rangle = \sum_i \sum_{w \in P_0^{(i)}} \lambda_i^2.$$  \hspace{1cm} (2.17)$$

For example, a pulse that evolves the system from the shifted and scaled density matrix

$$\rho_0' = \text{diag}(2, 0, 0, -2)$$  \hspace{1cm} (2.18)$$

to

$$\rho'(T) = \text{diag}(-2, 0, 0, 2)$$  \hspace{1cm} (2.19)$$

has freedom in mapping the subspace $|01\rangle, |10\rangle$ to itself due to the degeneracy of the eigenvalue 0. A general 2x2 unitary matrix has 4 real degrees of freedom, and after adding one more degree of freedom from the rest of the states, we have a total of 5. In conclusion, finding a pulse that implements a specific unitary matrix is more difficult than finding a pulse that applies a state to state transformation, and in the latter, a degeneracy of the density matrix eigenvalues makes the task even easier. The freedom of the polarization exchange pulse is analyzed more thoroughly in appendix F.
2.3.3 Initial Pulse

The optimization defines the initial and final density matrices, but the path of the system’s evolution is only limited indirectly by constraints such as the pulse duration and the rates of the interactions. Therefore, various pulses that maximize the efficiency usually exist. The local maximum of the target function found by algorithm is determined by the initial pulse, which can be either random or a pseudo-optimal pulse that the optimization will improve. In our system, only in highly constrained scenarios an initial pulse has failed to be optimized to a satisfying theoretical fidelity (≥0.99).

2.3.4 Total RF Energy Constraint

The total energy of the pulse might be limited by hardware or the sample allowed temperatures. GRAPE allows adding a penalty term to the target function which is proportional to the total energy of the pulse:
\[
\Phi_{RF} = -\alpha \sum_{j,k} |u_k(j)|^2 \Delta t. \tag{2.20}
\]

Where \(\alpha\) is a positive scalar that determines the weight of the penalty. A corresponding term is added to the gradient:
\[
\frac{\delta \Phi_{RF}}{\delta u_k(j)} = -2\alpha |u_k(j)| \Delta t. \tag{2.21}
\]

Choosing \(\alpha\) is done by trial and error. Too large \(\alpha\) will greatly reduce the fidelity or extend the pulse duration while too small \(\alpha\) would have no effect on the optimization.

2.3.5 Improving the Pulse Robustness to Parameters

Any experimental system deviates to some extent from its nominal parameters. It is desirable that the pulse designed would be robust to the expected range of these parameters. For example, say that the chemical shift spin #1 (\(\delta_1\)) was measured with accuracy of ±1 Hz. The chemical shift appear in the Hamiltonian, hence the fidelity \(\Phi\) depends on \(\delta_1\). In order to have a pulse which is robust to \(\delta_1 \in [-1, 1]\), we can modify the target function used by GRAPE:
\[
\Phi_{total} = \sum_{\delta_1 = -1, -1 + \Delta, \ldots, 1} \Phi(\delta_1). \tag{2.22}
\]

Where \(\Delta\) defines how fine the robustness to \(\delta_1\) would be. The gradient of \(\Phi_{total}\) is simply the sum of the gradients of each \(\Phi(\delta_1)\). Using this technique, the pulse can provide high fidelity over a wide range of parameters. Practically, it is advised not to choose too many parameter sets, in order to save computation time, and avoid an increase of the pulse duration.

2.4 GRAPE Implementation on SIMPSON

In 2009 a GRAPE implementation algorithm was added to SIMPSON [73], hence the SIMPSON program serves today both as a simulation program and as a pulse generation program. It is recommended to read this section with the examples at appendix G. We will repeat some of the information that was already mentioned in sub-section 2.1, to keep both sub-sections self contained.
2.4.1 The Input File

The input file to SIMPSON in OC mode is slightly different than in simulation mode:

1. **spinsys** - A structure that defines spin system parameters such as spin types, J-coupling constants, chemical shifts etc.

2. **par** - This structure defines parameters such as the initial and final density matrix, the pulse duration and number of sampling points of the pulse.

3. **pulseq** - A procedure that defines the pulse sequence.

4. **gradient** - A procedure called when the gradient in GRAPE is required.

5. **target_function** - A procedure called when the target function in GRAPE is required.

6. **main** - The first procedure run when the script starts. It prepares the initial guess of the pulse, and initiates the GRAPE algorithm. This procedure can be used to process and save the output data.

   **fsimpson** is a key procedure, which can be called in 2 different ways in the input file: When called from **gradient**, it returns the gradient of current pulse. When called from **target_function**, it evaluates the target function of the current pulse.

2.4.2 Typical Program Flow in Pulse Generation Mode

1. **main** prepares the initial guess of the pulses and calls **oc_optimize**.

2. **oc_optimize** runs the GRAPE algorithm:
   
   (a) **target_function** is called to evaluate the target function of the current guess.
   (b) **gradient** calculates the gradient of the current guess by calling **fsimpson**.
   (c) A line search is performed by calling **target_function** several times, in order to calculate the optimal step size $\eta$ defined in step 4 of GRAPE (see section 2.3.1).
   (d) Return to (b) until optimality conditions are met.

3. The control is returned to **main**, which saves the pulse.

2.4.3 Improving Robustness

Pulse robustness can be realized following the scheme in 2.3.5. The procedure **target_function** will call **fsimpson** multiple times to evaluate the target function with different parameter sets. Then, the different values are averaged, and **target_function** will return the average. **gradient** can be modified accordingly (See example at appendix G.2).

2.4.4 Robustness to RF Inhomogeneity

As the NMR probe transmits a pulse to the sample, not all areas of the sample receive the same intensity. That is called RF inhomogeneity. If the probe is multi-channel, the spatial distribution of the inhomogeneity might be different for each channel. The RF inhomogeneity profile that SIMPSON uses for robustness is defined in an additional file (see example in appendix G.3), unlike robustness for other parameters that is done manually.
2.5 Advantages of a Numeric Optimization

In the previous work on TCE [10], the pulses were designed manually, hence two key approximations were made to simplify the calculations. First, the weak $J_{\text{H,C}}$ coupling (See Figure 3.1) was neglected and second, the coupling between C1 and C2 was approximated by the Ising model (i.e., as if they are heteronuclear), although the condition $|\omega^{(C1)} - \omega^{(C2)}| \gg J_{C1,C2}$ was not met. Furthermore, calculating the pulse manually requires repeated refocusing pulses to avoid the undesired evolution due to chemical shifts and scalar coupling during the short waiting required in PT or compression. Utilizing GRAPE, we could use the accurate Hamiltonian, including chemical shifts, to achieve higher fidelity pulses.

The many control variables of the numerically optimized pulse allow all degrees of freedom of the quantum system and experimental apparatus to be utilized. Therefore, in comparison to pulse sequences designed as a concatenation of simple pulses or building blocks, the numerically optimized pulse generally allows shorter state to state evolution of the system [53].

Line selective and spin selective pulses are narrow bandwidth (soft) pulses utilized for various applications in NMR such as exciting or suppressing a specific energy transition (spectral line), or exciting specific spins [30]. By utilizing an amplitude and phase modulation, shaped pulses obtain spectral flexibility, thus incorporating line and spin selective pulses.

Pulse sequences such as INEPT [51] suppress unwanted signals of the native polarization from the spectrum, by multi-scan experiments, transmitted in alternating phases. Using GRAPE, the native polarization can be treated without multiple scans, by properly defining the initial and final density matrix, so that unwanted polarization would not interfere with the desired signal. Phase cycling solves another problem - imbalanced amplification of the X and Y channels in the heterodyne circuit of the transmitter. Additional optimization is required to generate a pulse that is robust to this imbalance.

Unlike numerically optimized pulses, INEPT and similar pulse sequences are sensitive to miscalibration and to RF inhomogeneity. A mere 5% power deviation of a 90° pulse reduces its efficiency to $\sin(0.95\frac{\pi}{2}) = 0.997$. A refocused INEPT which consists of 7 pulses (on both channels) will have an approximated efficiency of $0.997^7 = 0.98$, before dephasing effects are taken into account. A more complex pulse sequence which consists of 28 pulses will degrade to 0.92 efficiency under these conditions. Therefore, the robustness of the pulses generated by SIMPSON was expected to significantly improve the efficiency of complex pulses required for AC (e.g., compression).

It is important to stress that without optimal control, the efficiency of the compression pulse was too low to be used.
Chapter 3

Materials and Methods

This chapter describes the working procedures and methods developed to generate the pulses utilized in the experiment.

3.1 Equipment

The experiments were performed on a Bruker Avance III 600 spectrometer using a standard 5 mm BBO probe. The sample was $^{13}\text{C}_2\text{-TCE}$ with paramagnetic reagent $\text{Cr(acac)}_3$, in CDCl$_3$ (chloroform-d) solution (see Figure 3.1). Table 3.1 summarizes the $T_1$ and $T_2^*$ values of the spin system.

![Figure 3.1: Three spins in $^{13}\text{C}_2\text{-TCE}$ were utilized in the experiment: H, C2, and C1. In the table, the chemical shifts relative to the transmitter frequency are in the diagonal elements, and the J-couplings are in the off diagonal elements. Note that the broadcasting frequency of the carbon channel is between the Larmor frequencies of C1 and C2. The carbon spectrum is at the bottom, the proton spectrum is in the small frame. Remark: The carbons have different $T_2^*$, hence their peaks have different heights, although their integrals are equal up to an error of 0.02.](image)

$T_2^*$ was measured directly from the spectrum (single scan, line-width at half maximum). $T_1$ of each
spin was measured in a different experiment, a few days earlier, by a standard inversion recovery method (Bruker pulse program: \texttt{t1ir}). Typically, 17 logarithmically evenly spaced delays were used, and $T_1$ was found by fitting the data to the expected exponential model. Remark: the temperature stabilizer was malfunctioning during the experiment causing a temperature drift, and an additional error to the $T_1$ measurements.

<table>
<thead>
<tr>
<th></th>
<th>$H$</th>
<th>$C2$</th>
<th>$C1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_1$ (sec)</td>
<td>$2.67 \pm 0.03$</td>
<td>$17.3 \pm 0.2$</td>
<td>$29.2 \pm 0.1$</td>
</tr>
<tr>
<td>$T_2$ (msec)</td>
<td>$200 \pm 10$</td>
<td>$440 \pm 30$</td>
<td>$230 \pm 10$</td>
</tr>
</tbody>
</table>

Table 3.1: Measured $T_1$ and $T_2$ values of TCE.

In the carbon channel, we chose to broadcast between the Larmor frequencies of the two carbons. While choosing to broadcast on one carbon, say C1, would have made its control easier, the control of C2 will become much difficult as we transmit 1khz off its Larmor frequency. Although the bandwidth of the pulse is bounded by the $\Delta t$ between the control points, and is roughly 1 Mhz, we feared the excess modulation will reduce the pulse efficiency.

### 3.2 Pulse Design Basics

#### 3.2.1 Acquiring the Hamiltonian Parameters

SIMPSON requires the full Hamiltonian of the system, namely, the J-coupling constants and the chemical shifts of the spins. J-coupling constants were found directly from the spins’ excitation (90°) spectra, i.e., by using Bruker \texttt{zg} pulse program. However, the carbons Larmor frequencies are close compared to their J-coupling, hence, the difference between their Larmor frequencies is not the frequency difference between the center of their lines. We preferred to calculate their chemical shifts by matching the measured spectrum in the lab to the predicted spectrum of TCE using SIMPSON in simulation mode (see appendix C). After collecting the parameters measured, the rotating frame Hamiltonian used for the optimization is (coupling constants and chemical shifts are in Hz):

$$H = 2\pi \hbar (541.7I_z^C1 - 541.7I_z^C2 + 200.8I_z^C1I_z^H + 103.1I_z^C1I_z^C2 + 9I_z^C1I_z^H)$$

(3.1)

#### 3.2.2 Noteworthy SIMPSON Parameters

The following parameters should be set carefully when designing a new pulse:

1. **Maximum amplitude (maxRF)**\(^2\)\(^3\) of the pulse should not pass the operational limits of the probe or the amplifier. An amplifier’s linearity depends on its dynamic range, hence choosing a low maximal amplitude may improve the fidelity of the pulse, as well as reduce the heating of the sample. On the other hand, too low value may constrain the pulse and increase its duration. The amplitude limit was set to 2 kHz on both channels (which translates to 23.5db for the carbon channel and 17db for the hydrogen channel).

2. **Pulse duration (duration)** is chosen to be as short as possible to reduce thermalization and dephasing, while allowing the interactions to evolve the spin system long enough to complete the

---

\(^1\)In \texttt{t1ir} (inversion recovery) sequence, a 180° pulse is applied, followed by a varying delay $\tau$, 90° pulse and acquisition.

\(^2\)In parentheses is the name of the variable in the script file.

\(^3\)Custom parameter, not part of the principle parameters of SIMPSON.
density matrix transition as desired. In practice, no analytical calculation was done, and the minimal pulse duration was found by running SIMPSON with decreasing pulse durations, until the fidelity began to deteriorate. Note that adding constraints may increase the pulse duration.

3. **Number of control points (NOC).** Empirically, the efficiency improves with the number of elements, therefore this parameter is set to 5000, the maximum allowed by the program due to memory consumption.

4. **RF inhomogeneity (rfprof_file)** increases the efficiency observed in the lab. However, increasing the range of inhomogeneity robustness causes the pulse to be longer, and increases the run time of SIMPSON. The RF profile chosen is $\pm 15\%$ uniformly distributed inhomogeneity in both channels (see appendix G.3).

5. **Total energy constraint weight (lam)** is the parameter $\alpha$ described in section 2.3.4. We observed that the optimization run time was reduced when increasing this parameter, and that the pulse becomes more smooth. On the other hand, the pulse duration may increase by this additional constraint on the control variables.

6. **Initial density matrix (start_operator) and desired density matrix (detect_operator),** both shifted and scaled, are defined using strings such as “I1z+I2z”. The spins index is by the order the spins are defined in the *spinsys* structure. The matrices should have the same eigenvalues to allow a unitary transformation between them. Section 3.3 describes in detail the considerations in selecting these parameters for the pulses designed.

### 3.2.3 Sensitivity Estimation Using the SIMPSON Simulation

Once a pulse was generated it is possible to see how sensitive it is to various parameters by evaluating the target function of the pulse with parameters deviating from the nominal. Knowing the sensitivity of a parameter is utilized for determining how much effort should be made in tuning or measuring it. The required robustness of the pulse to this parameter is also deduced from the sensitivity. Table 3.2 summarizes the sensitivity to different parameters of the compression pulse, with expected nominal fidelity of 0.9985.

*Sensitivity that originates from thermalization or dephasing will not be accurately estimated since SIMPSON does not take them into account. Also, sensitivity to a combination of variables was not tested.*
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Nominal Value</th>
<th>Deviated Value</th>
<th>Expected Fidelity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen resonance frequency</td>
<td>600.55 MHz</td>
<td>606.13 MHz</td>
<td>0.9958</td>
</tr>
<tr>
<td>(Principle magnetic field inhomogeneity)</td>
<td></td>
<td>594.55 MHz</td>
<td>0.9956</td>
</tr>
<tr>
<td>$J_{H,C_2}$</td>
<td>201 Hz</td>
<td>221 Hz</td>
<td>0.9862</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180 Hz</td>
<td>0.9841</td>
</tr>
<tr>
<td>$J_{C_1,C_2}$</td>
<td>103 Hz</td>
<td>113 Hz</td>
<td>0.9912</td>
</tr>
<tr>
<td></td>
<td></td>
<td>93 Hz</td>
<td>0.9891</td>
</tr>
<tr>
<td>$J_{H,C_1}$</td>
<td>9 Hz</td>
<td>12 Hz</td>
<td>0.9983</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5 Hz</td>
<td>0.9984</td>
</tr>
<tr>
<td>Pulse duration</td>
<td>13 msec</td>
<td>13.2 msec</td>
<td>0.9918</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.8 msec</td>
<td>0.9907</td>
</tr>
<tr>
<td>Hydrogen frequency miscalibration</td>
<td>0</td>
<td>+20 Hz</td>
<td>0.9887</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-20 Hz</td>
<td>0.9911</td>
</tr>
<tr>
<td>Carbon frequency miscalibration</td>
<td>0</td>
<td>+20 Hz</td>
<td>0.9735</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-20 Hz</td>
<td>0.9692</td>
</tr>
<tr>
<td>Difference between the carbons' Larmor frequencies</td>
<td>1083 Hz</td>
<td>1103 Hz</td>
<td>0.9922</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1063 Hz</td>
<td>0.9917</td>
</tr>
</tbody>
</table>

Table 3.2: Estimated sensitivity of the compression pulse to parameters. The expected fidelity for nominal parameters is 0.987.

### 3.2.4 The Effect of Thermalization and Dephasing on the Pulse Efficiency

SIMPSON does not take dissipation mechanisms into account. This is one of the reasons the observed efficiency of the designed pulses in the lab is smaller than the efficiency predicted by SIMPSON. The dissipation rates of a system depend on its state. For example, when a spin is on the x axis it will experience $T_2$ relaxation and eventually the slower $T_1$ relaxation, while on the z axis it experience only the $T_1$ relaxation. Even pulses which apply the same unitary operator might evolve the system in different paths that will cause a different amount of dissipation, and will therefore have different fidelities. A full analysis of the dissipation processes in TCE is beyond the scope of this work. Therefore, the uncertainty of the pulse fidelity in the lab was dealt with by generating several pulses that apply the same operation (state to state), and picking the pulse with best fidelity in the lab. In future work, an analysis of dissipation processes can be done in order to find an optimal path. The pulse can be prepared by tailoring multiple pulses (generated by SIMPSON) that evolve the system through states in the optimal path.

### 3.3 Designing Building Blocks of AC Using SIMPSON

The fine details of each pulse’s design are described in this section. The computation of the pulses required hundred of iterations of the optimization, and hours or even days of computer time, depending on the complexity of the pulse and its constraints. In order to reduce the calculation time, the pulse was first optimized without RF robustness, to reach the vicinity of the efficient pulses. Then, robustness constraint
was added to the optimization, improving the pulse further (but vastly increasing the calculation time of each iteration).

The design of the compression and PE pulses has proven to be very challenging. Both pulses are applied multiple times during AC, to a system in a different state each round, hence pulses applying unitary transformation (e.g., 3BC, SWAP) would be ideal. However from our experience in the lab, pulses designed to apply a specific unitary matrix had poor performance, and we resorted to using state to state pulses. Appendix F shows the general form of the unitary matrices applying PE. Due to the difficult and long process of pulse design, instead of tailoring a specific compression and PE pulses to each round of cooling (the initial state of the system changes each round), we chose to use the same two pulses for all the rounds of AC. We will justify this decision in the next sections.

3.3.1 Polarization Exchange Pulse

A polarization exchange pulse swaps the polarizations of H and C2, without changing the polarization on C1, as required by the algorithm.

The PE pulse was generated with the following SIMPSON parameters:

- **start_operator**: $I_z^{C1} + I_z^{C2} + 4I_z^H \propto \text{diag}(6, -2, 4, -4, 4, -4, 2, -6)$
- **detect_operator**: $I_z^{C1} + 4I_z^{C2} + I_z^H \propto \text{diag}(6, 4, -2, -4, 4, 2, -4, -6)$
- **rfprof_file**: rf_file2d15% (see G.3)
- **maxRF**: 2 KHz
- **duration**: 6 msec

SIMPSON yields the expected unitary matrix of the pulse. The following table\textsuperscript{5} illustrates how the pulse affects the spin system. Non diagonal elements are ignored as $T_2$ is much smaller than the WAIT times. Note that 0.995 of the proton’s polarization is transferred to C2, while C1 loses 2.4% of its polarization, and that other product operators weakly interfere with the polarization of C1 and C2. Therefore, it is important to stress that the pulse is efficient when applied on density matrices other than the initial density matrix it was designed for.

\textsuperscript{5}See appendix H for a simple example of the unitary tables.
Table 3.3: An illustration of the predicted unitary matrix of the polarization exchange pulse. In each row, the pulse is applied on a diagonal product operator and then projected on the product operators in the columns. Only significant terms of the result are displayed. For example $U_{pe} I_z^H U_{pe}^\dagger \approx 0.995 I_z^C$. The blue underlined entries illustrate the transitions important for PE.

For comparison, the ideal SWAP gate is:

Table 3.4: A SWAP gate. In each row, the pulse is applied on a diagonal product operator and significant terms of the result are displayed.

Another special case of polarization exchange is refocused-INEPT:

Table 3.5: Refocused-INEPT: CNOT(C2,H) followed by CNOT(H,C2). In each row, the pulse is applied on a diagonal product operator and significant terms of the result are displayed.

40
3.3.2 Compression Pulse

Although infinite number of possible compression pulses maximize the polarization of C1, several considerations were made when selecting the final density matrix. It is desirable that at the end of the compression, C2 and H would retain some of their polarization, in order to reduce the reset times of the hydrogen in the next steps of AC. Density matrix terms with long thermalization time such as $I_z^C I_z^C$ were avoided as they don’t vanish before the next PE step, and may hinder the cooling. Note that the coupling constants determine the transition times, hence choosing a final density matrix determines the pulse length, indirectly affecting the efficiency. We chose a final density matrix which is identical to the result of applying 3BC on the initial density matrix. The compression pulse was generated with the following SIMPSON parameters:

1. **start_operator**: $I_z^C + I_z^C + I_z^H \propto \text{diag}(3, 1, 1, -1, 1, -1, -1, -3)$

2. **detect_operator**: $1 \frac{1}{2} I_z^C + \frac{1}{2} I_z^C + \frac{1}{2} I_z^H + 2 I_z^H I_z^C I_z^C \propto \text{diag}(3, 1, 1, -1, -1, 1, -1, -3)$

3. **rfprof_file**: rf_file2d15% (see G.3)

4. **maxRF**: 2 kHz

5. **duration**: 13 msec

The following table illustrates how the pulse affects the spin system. Surprisingly, the final pulse generated (see Table 3.6) is valid for any cooling round, as it transforms half the polarization of each of the spins independently to C1. It remains an open question why the optimization converged to a pulse with such a beneficial quality. Note the tri-linear term emerging when the pulse is applied to the equilibrium state, which is later taken into account in the AC simulation at section 4.2. The amplitude of the compression pulse on the carbon channel is shown in 3.3.

<table>
<thead>
<tr>
<th></th>
<th>$I_z^H$</th>
<th>$I_z^C$</th>
<th>$I_z^C$</th>
<th>$I_z^H I_z^C$</th>
<th>$I_z^C I_z^C$</th>
<th>$I_z^H I_z^C$</th>
<th>$I_z^H I_z^C I_z^C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U_{\text{Comp}} I_z^H U_{\text{Comp}}^\dagger$</td>
<td>0.423</td>
<td>-0.414</td>
<td><strong>0.5</strong></td>
<td>0.15</td>
<td>-0.137</td>
<td>1.96</td>
<td></td>
</tr>
<tr>
<td>$U_{\text{Comp}} I_z^C U_{\text{Comp}}^\dagger$</td>
<td>-0.385</td>
<td>0.434</td>
<td><strong>0.499</strong></td>
<td>0.02</td>
<td>-0.12</td>
<td>0.102</td>
<td>1.80</td>
</tr>
<tr>
<td>$U_{\text{Comp}} I_z^C I_z^C U_{\text{Comp}}^\dagger$</td>
<td>0.462</td>
<td>0.480</td>
<td><strong>0.499</strong></td>
<td>-0.024</td>
<td>0.036</td>
<td>-1.768</td>
<td></td>
</tr>
<tr>
<td>$U_{\text{Comp}} I_z^H I_z^C U_{\text{Comp}}^\dagger$</td>
<td>-0.009</td>
<td>0.006</td>
<td>0.941</td>
<td>0.038</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$U_{\text{Comp}} I_z^C I_z^C U_{\text{Comp}}^\dagger$</td>
<td>0.04</td>
<td>-0.04</td>
<td>0.914</td>
<td>0.076</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$U_{\text{Comp}} I_z^H I_z^C I_z^C U_{\text{Comp}}^\dagger$</td>
<td>-0.026</td>
<td>0.03</td>
<td>0.05</td>
<td>0.065</td>
<td>0.884</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$U_{\text{Comp}} I_z^C I_z^C I_z^C U_{\text{Comp}}^\dagger$</td>
<td>0.125</td>
<td>0.125</td>
<td>-0.125</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.6: An illustration of predicted unitary matrix of the compression pulse. In each row, the pulse is applied on a diagonal product operator and significant terms of the result are displayed. For example $U_{\text{Comp}} I_z^H I_z^C I_z^C U_{\text{Comp}}^\dagger \approx 0.125 \left( I_z^H + I_z^C - I_z^C \right) + 0.5 I_z^H I_z^C I_z^C$. Note that the pulse transforms half the polarization of each of the spins independently to C1 (underlined entries colored blue).
For comparison, the transformation of 3BC is

\[
U = \begin{pmatrix}
1 & 1 & 1 \\
0 & 1 & 1 \\
1 & 0 & 1 \\
1 & 1 & 1
\end{pmatrix}
\]

(3.2)

where in the Hilbert space, the LSB is H; the middle spin is C2 and C1 is the MSB. 3BC corresponds to the following table:
Table 3.7: A 3-bit compression pulse. In each row, the pulse is applied on a diagonal product operator and significant terms of the result are displayed.

A different compression scheme is to apply CNOT(C2,H) and then if H is 0, apply SWAP (C1,C2).

Table 3.8: A CNOT(C2,H) followed by CSWAP (H; C1 ↔ C2). In each row, the pulse is applied on a diagonal product operator and significant terms of the result are displayed.

Figure 3.2 shows the phase and amplitude of the part of the compression pulse applied to the carbon channel. Note that the rapid modulation of the amplitude and phase during the pulse are not always feasible by the hardware, thus reducing the pulse efficiency. The Fourier transform of the pulse’s x component is shown in figure 3.3. It is difficult to understand from this image how the pulse addresses the two carbons.
Figure 3.2: The shape of the compression pulse on the carbon channel. In the top graph, the vertical axis is the RF amplitude, limited by $\text{maxRF}$ and the horizontal axis is the time (the total time of the pulse is 13 msec). The bottom graph shows phases of the same pulse (in degrees).
Figure 3.3: Fourier transform of the x component of the compression pulse applied to the carbons. The spectral width is about 50 kHz.

3.3.3 Selective Excitation Pulse on C2

A selective pulse on C2 was designed as a utility pulse, i.e., not part of the algorithm, in order to calibrate the power level of the carbon channel’s shaped pulses (further details in section 3.4.2). The pulse assumes a system on equilibrium and rotates C2 to the x axis, leaving C1 at the z axis. Only the carbon channel is irradiated. The optimization parameters are\(^6:\)

- **start_operator**: \(I_z^{C1} + I_z^{C2} \propto \text{diag}(2, 2, 0, 0, 0, 0, 0, 2, -2)\)
- **detect_operator**: \(I_z^{C1} + I_z^{C2}\)
- **duration**: 1 msec
- **maxRF**: 2 kHz
- **RF inhomogeneity**: 20\% (steps: 0.8, 0.85...1.2)
- **lam**: 0.5e-5

Figure 3.4 shows a typical spectrum when the power level of the carbon channel is calibrated. The integral over C1 is \(0.01 \pm 0.02\) and the integral over C2 is \(1.00 \pm 0.02\) compared to the \(zg\) spectrum.

3.4 Experiment Preparation

Before each lab session, two key procedure were preformed: acquiring reference spectra and calibrating the power levels of the pulses.

\(^6\)Note that the proton was omitted from the density matrix as it is not affected by the carbon channel.
3.4.1 Acquiring Reference Spectra

The efficiency of a pulse or an algorithm is determined by comparing the outcome polarization of the spins with their equilibrium polarization. The polarization is proportional to the integral over the spin’s spectral lines following a $\left[ \frac{\pi}{2} \right]_y$ pulse (see appendix B.1), and therefore the efficiency is determined by comparing the integral after the pulse or AC to the integral after an excitation ($\left[ \frac{\pi}{2} \right]_y$) pulse on the system in equilibrium. The spectrum of the carbons following a calibrated $\left[ \frac{\pi}{2} \right]_y$ hard pulse (15.05 µsec) is shown in Figure 3.5. An excitation spectrum (15 µsec pulse) of the proton is shown in Figure 3.6. We tried to have the reference spectra acquired next to the AC experiments to avoid any drift effects.

---

7These spectra were displayed earlier in Figure 3.1.
3.4.2 Power Calibration

The pulse generated by SIMPSON is given in nutation frequency units (Hz), which should be converted to the attenuation of the transmitter in the lab (db). When the pulse is applied on two channels, both should be calibrated. The carbon channel was calibrated using a 5 msec selective pulse, generated by SIMPSON, which rotates C2 to the x axis while keeping C1 on the z axis (see section 3.3.3). The pulse was transmitted in different power levels. The power level selected is the one that gave the minimal integral over C1, while the integral over C2 was close to the corresponding integral in the spectrum of a calibrated hard excitation ($90^\circ$) pulse. Knowing the carbon calibration, the power level of the hydrogen
in the polarization exchange pulse was calibrated by finding the power which maximizes the polarization transferred to C2. Due to the pulse robustness to RF inhomogeneity, the efficiency of the pulses during calibration were often high over an RF power range of ±0.2db (±2.3%).

3.5 Spectra of Polarization Exchange and Compression Pulses

The spectrum measured when applying the selected PE pulse and a readout pulse on equilibrium state is displayed in Figure 3.7. The measured polarization of C1 and C2 are 0.98±0.02 and 3.76±0.02 respectively. The transfer efficiency is therefore 94%, and the loss of C1 polarization is close to the prediction. Figure 3.8 shows the spectrum of the carbons following the compression pulse and a readout pulse. The polarizations of C1 and C2 are 2.76±0.02 and -0.631±0.02 respectively, while the SIMPSON prediction is 3 and -0.73. The efficiency of the compression pulse, which refers to the acquired polarization of C1 is 92%.

Figure 3.7: The spectrum of the carbons after applying polarization exchange, followed by a non-selective 90° pulse. The intensities of C1 and C2 are 0.98 ± 0.02 and 3.76 ± 0.02 respectively, compared to a calibrated zg spectrum.
Figure 3.8: The spectrum of the carbons after applying a compression pulse, followed by a non-selective $90^\circ$ pulse. The intensities of C1 and C2 are $2.76 \pm 0.02$ and $-0.631 \pm 0.02$ respectively, compared to a calibrated zg spectrum.
3.6 SIMPSON’s Predicted Efficiency vs Observed Efficiency

The pulses generated by SIMPSON have very high predicted efficiency (> 0.99). The following factors may explain the gap between SIMPSON’s predicted pulses efficiency, and the efficiency observed in the lab which was between 92% to 94%.

1. Dephasing - throughout the evolution of the density matrix during the pulses, the system may experience different dephasing which depends on its instantaneous state. Assuming dephasing time constant is the spins’ average $T_2^*$, 290 ms, the polarization lost during a 6 msec pulse and a 13 msec pulse is (very) roughly 2% and 4% respectively. A deeper analysis of the evolution of the density matrix is required for a better estimation.

2. The probe and the rest of the hardware has limited bandwidth [6,63] and therefore attenuates and distorts frequencies that are far from the carrier wave (see Topspin’s wobb command for the probe’s respond). In our case, the distance between the control points of the shaped pulses is roughly a few micro-seconds, which translates to a bandwidth of $\approx$1 Mhz. Therefore, a highly modulated pulses may reach lower efficiencies than smooth pulses.

3. The number of the pulse’s control points (NOC parameter) seems to affect the observed efficiency. Although the maximal number of control points were used, an internal numerical error, possibly an accumulated error, may still reduce the efficiency.

4. RF inhomogeneity robustness seems to improve the efficiency greatly. It is not certain whether such an RF inhomogeneity exists or that the robustness compensates for other errors.
Chapter 4

Entropy Reduction via Algorithmic Cooling in Liquid State NMR

In this chapter we present the design of the algorithm, given the prepared pulses, and the expected results.

4.1 Implemented Cooling Algorithms

The base experiment implemented (denoted as “experiment A”) was aimed to maximize the polarization of C1. In each round, the proton relaxes from the previous round (see D3 delay in Figure 4.1), the polarizations of the proton and C2 are swapped by a PE pulse, and after the proton relaxes again (D2 delay), the round is concluded by applying a 3-bit compression to cool C1. C1 becomes colder each round, in diminishing increments, until the change becomes undetectable. Before acquisition, another pulse is applied on the spins to rotate their polarizations to the XY plane, making their polarizations visible in the spectrum. Practically, C1 and C2 experience $T_1$ relaxation during the reset steps, and so the theoretical limit of cooling by a factor of 8 is not reachable. Our simulation in section 4.2 shows that given these thermalization times and assuming perfect pulses, the polarization of C1 could be enhanced by a factor of 5.67.

The PE and compression pulses were generated using SIMPSON version 3.0 [5, 73], an open source program implementing GRAPE. We used SIMPSON’s state to state mode, that produces pulses evolving the spin system from a given initial density matrix to a given final density matrix. In this mode, the optimization algorithm is not bounded to a specific unitary matrix, hence allowing shorter pulses, reducing dephasing during the pulse and reaching higher efficiencies. However this freedom may cause an undesired transformation when applied in different cooling rounds as the density matrices change from round to round. Instead of tailoring specific compression and PE pulses to each round of cooling, we chose to use the same two pulses for all the rounds of AC, and as shown in section 3.3, the pulses are adequate for application in multiple rounds. Since the SIMPSON optimization doesn’t consider dissipation processes as well as the limitation on the hardware’s bandwidth, the pulses generated had inherent error. To address the problem, we generated many different pulses with the same parameters, and picked the ones that gave the best efficiency in the lab.

Once efficient pulses were prepared, the wait times during reset - i.e., the wait before PE (D3), and between PE and the compression (D2) were optimized to maximize the cooling of C1. Generally the wait
times could vary between rounds, but we chose to use the same D2 and D3 in all the cooling rounds, assuming the same maximal cooling of C1 will be reached, but perhaps by more rounds. The delay times D2 and D3 were optimized by applying multi round AC with initial guesses of delays; the delays were then varied, following the steepest ascent of the C1 cooling, until a maximal cooling was reached (see Table 4.1). The optimal wait periods found are D2=3s, D3=5s.

<table>
<thead>
<tr>
<th>D2 \ D3</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
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<tr>
<td>2</td>
<td>4.54,1.77</td>
<td>4.57,1.77</td>
<td>4.59,1.77</td>
<td>4.56,1.74</td>
<td>4.55,1.71</td>
</tr>
<tr>
<td>3</td>
<td>4.54,1.77</td>
<td>4.57,1.77</td>
<td>4.59,1.77</td>
<td>4.56,1.74</td>
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</tr>
<tr>
<td>4</td>
<td>4.58,1.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4.57,1.5</td>
<td>4.57,1.47</td>
<td></td>
<td></td>
<td>4.52,1.42</td>
</tr>
</tbody>
</table>

Table 4.1: The cooling factors of C1 and C2 following 10 rounds of AC, with different D2, D3. The measurement error is ±0.02.

On experiment B, a WAIT step (D6) and a polarization exchange step were applied before the readout pulse of experiment A. This way both carbons are cooled since the polarization of C2 is enhanced while C1 slowly losing part of the high polarization it gained. The same pulses and wait periods as experiment A were used, however D6 was optimized separately.

On experiment C, we started with experiment A, but before the readout pulse, we waited (D6), applied PE, and waited again (D4) - allowing the proton to regain some of its polarization while the carbons are slowly losing part of theirs. This way the IC of the entire spin system is maximized. The two last waits were optimized separately.

4.2 Simulation of the Algorithm

4.2.1 Analysis

A simulation of the algorithm was written in order to evaluate the quality of our results and for verification. The simulation assumes ideal SWAP and 3bit-compression (3BC) pulses, as well as a limited
model of thermalization, i.e. that spins thermalize independently\(^1\). No off-diagonal elements emerge when applying the pulses or during WAIT steps, hence we can ignore these terms in the simulation. The diagonal terms to consider, beside the linear terms representing the polarizations, depends on the compression step of the algorithm and the correlation term it creates (as WAIT and SWAP create no correlation). When applying 3BC on TCE with polarizations \(\varepsilon_{C1}, \varepsilon_{C2}\) and \(\varepsilon_H\) (and only linear terms in the density matrix), the polarization on \(C_1\) becomes \(\frac{1}{2} (\varepsilon_{C1} + \varepsilon_{C2} + \varepsilon_H)\), and a tri-linear term emerges:

\[
U \left( \varepsilon_{C1} I_z^{C1} + \varepsilon_{C2} I_z^{C2} + \varepsilon_H I_z^H \right) U^\dagger = \frac{\varepsilon_{C1} + \varepsilon_{C2} + \varepsilon_H}{2} I_z^{C1} + \frac{\varepsilon_{C1} + \varepsilon_{C2} - \varepsilon_H}{2} I_z^{C2} + \frac{\varepsilon_{C1} - \varepsilon_{C2} + \varepsilon_H}{2} I_z^H - 2 (\varepsilon_{C1} + \varepsilon_{C2} + \varepsilon_H) I_z^{C1} I_z^{C2} I_z^H.
\]

(4.1)

When applying \(U\) on the tri-linear term, no new diagonal element emerges:

\[
U I_z^{C1} I_z^{C2} I_z^H U^\dagger = \frac{1}{8} (-I_z^{C1} + I_z^{C2} + I_z^H) + \frac{1}{2} I_z^{C1} I_z^{C2} I_z^H.
\]

(4.2)

SWAP(H,C2) is applied by the following propagator:

\[
U = \begin{pmatrix}
1 & 0 & 1 \\
0 & 1 & 0 \\
1 & 1 & 1 \\
0 & 1 & 0 \\
1 & 0 & 1
\end{pmatrix}
\]

(4.3)

The SWAP gate has no effect on the \(I_z^{C1} I_z^{C2} I_z^H\) operator, and, as expected, swaps the polarizations of H and C2. Hence SWAP doesn’t add bilinear terms to the density matrix and only 4 elements participate in the simulation - \(I_z^{C1}, I_z^{C2}, I_z^H\) and \(I_z^{C1} I_z^{C2} I_z^H\). Note that when replacing SWAP by INEPT and/or for a different compression propagator, the simulation will consist of different elements.

During WAIT steps the polarizations relax by \(T_1\) relaxation:

\[
\varepsilon_H(t) = (\varepsilon_H(0) - \varepsilon_{H,eq}) e^{-t/T_{H,1}} + \varepsilon_{H,eq}
\]

\[
\varepsilon_{C2}(t) = (\varepsilon_{C2}(0) - \varepsilon_{C2,eq}) e^{-t/T_{C2,1}} + \varepsilon_{C2,eq}
\]

\[
\varepsilon_{C1}(t) = (\varepsilon_{C1}(0) - \varepsilon_{C1,eq}) e^{-t/T_{C1,1}} + \varepsilon_{C1,eq}.
\]

(4.4)

The coefficient of \(I_z^{C1} I_z^{C2} I_z^H\) decays exponentially with a time constant \(\tau\) and independently from the linear terms (see proof at appendix K):

\[
\frac{1}{\tau} = \frac{1}{T_{H,1}} + \frac{1}{T_{C2,1}} + \frac{1}{T_{C1,1}}.
\]

(4.5)

### 4.2.2 Predictions

According to the simulation, the optimal values of D2 and D3 are 2s and 3s respectively. Table 4.2.2 shows the expected polarizations throughout experiment \(A\) using these wait times. The maximal cooling

\[^1\text{In the lab we observed that this assumption was not accurate (see appendix J).}\]
reachable for C1 is 5.67.

In experiment B, the maximal predicted IC of C1 and C2 is 39.25, when waiting 3s after the cooling rounds of experiment A. The polarizations of C1 and C2 in this scenario are 5.22 and 3.47 respectively.

In experiment C, the maximal predicted IC of C1, C2 and H is 44.56, when waiting 1 sec before the 90° pulse of the optimized experiment B. The polarizations of C1, C2 and H in this scenario are 5.08, 3.33 and 2.77 respectively.
<table>
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<tr>
<th></th>
<th>$\varepsilon_{C1}$</th>
<th>$\varepsilon_{C2}$</th>
<th>$\varepsilon_H$</th>
<th>$T_1^C T_2 C_z^H$</th>
<th>IC(C1)</th>
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</thead>
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<td>0</td>
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<td>-0.042</td>
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<td>2.67</td>
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<td>1</td>
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<tr>
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<td>1.43</td>
<td>1.52</td>
<td>-4.26</td>
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</tr>
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<td>1.36</td>
<td>3.18</td>
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<td>1</td>
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<td>3.18</td>
<td>1.36</td>
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<td>2.74</td>
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<td>-4.07</td>
<td>22.75</td>
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</tr>
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<td>1</td>
</tr>
<tr>
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</tr>
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<td>2.25</td>
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<td>3.15</td>
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<td>2.40</td>
<td>-2.97</td>
<td>32.19</td>
</tr>
</tbody>
</table>

Table 4.2: Simulation of the state of the spin system and the information content of C1 during experiment $A$, assuming perfect pulses. Compare to table 1.2 which also assumes infinite $T_1$ ratios. Remark: when taking $\varepsilon_H = 4$ in equilibrium, the final compression yields $\varepsilon_{C1} = 5.70$, IC(C1)=32.48, $\varepsilon_{C2} = 2.47$, $\varepsilon_H = 2.42$ and the trilinear term coefficient is -2.99.
Chapter 5

Results

The polarizations of the spins following AC were measured by applying a readout pulse and by measuring the integral over the peaks of each spin. In each of the following results, the spectrum after AC, as well as the calibration spectrum, were acquired several times and for each spectrum, the integral over the spectral lines of the spins was measured separately, to estimate the measurement error. The spectrometer can only acquire the fid of one channel at a time, hence when both carbon and proton spectrum were required, they were measured in a two separate experiments. The estimated error of the integral over the carbons’ spectral lines is 0.02 in units of the carbon’s equilibrium polarization. The error of the integral over the hydrogen is 0.01 in the units of the hydrogen’s equilibrium polarization. The expressions for the information content (in units of $\varepsilon_c^2/\ln 4$) and for its error are:

\[
IC = \varepsilon_H^2 + \varepsilon_{C1}^2 + \varepsilon_{C2}^2 \quad (5.1)
\]

\[
\Delta IC = 2\varepsilon_H^2 \Delta \varepsilon_H^2 + \varepsilon_{C1}^2 \Delta \varepsilon_{C1}^2 + \varepsilon_{C2}^2 \Delta \varepsilon_{C2}^2 \quad (5.2)
\]

Note that correlation terms hold additional information content, which is not included in the calculation. Therefore, this expression for IC is a lower bound on the true IC of the system.

5.1 Experiment A

Table 5.2 shows the polarization build up on the carbons with the rounds of cooling in experiment A. The asymptotic limit is reached after 6 cycles. C1 was cooled by a factor of $4.61 \pm 0.02$, with $21.2 \pm 0.2$ information content, 19% higher than 17.84, the IC of the entire spin system at equilibrium\(^1\) (see Figure 5.1). It remains an open question whether using different delays in each round can improve the results even further.

---

\(^1\)IC is calculated here using the exact gyromagnetic ratios: $\gamma_{H,eq} = 3.98$. 

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Figure 5.1: Spectra of the carbon channel before and after experiment \( A \).
Table 5.1: The measured polarizations of the carbons and their IC after experiment $\mathcal{B}$ with various D6 delays.

Polarization of $3.78 \pm 0.02$ and $3.40 \pm 0.02$ of C1 and C2 respectively were measured, which summed up to IC of $25.9 \pm 0.2$ (see Figure 5.3)
Figure 5.3: Spectra of the carbon channel before and after experiment $B$. The measured integrals of the equilibrium spectrum at the top are calibrated to $1.00 \pm 0.02$ for both carbons. The measured integrals at the bottom spectrum are $3.78 \pm 0.02$ and $3.40 \pm 0.02$ for C1 and C2 respectively. The spectra are to scale with each other.
5.3 Experiment $C$

In experiment $C$, (conducted much later than $A$ and $B$, when the sample was potentially subjected to a small degree of degradation), where we aimed to maximize the IC of the entire spin system, the optimal delays found were $D_6=6s$, $D_4=6s$. The respective polarizations measured were $2.87 \pm 0.02$, $2.64 \pm 0.02$ and $3.58 \pm 0.02$ for C1, C2 and H respectively, summing to a total IC of $28.0 \pm 0.2$. See figure 5.4. For comparison, the total IC after POTENT was $20.70 \pm 0.06$.

![Figure 5.4: Spectra measured after experiment $C$. The proton spectrum (top) is calibrated such that the integral over all lines equals 1 at equilibrium excitation. The carbon spectrum is at the bottom.](image-url)
Chapter 6

Discussion

In this work we demonstrated AC in liquid state NMR, a step towards employing AC in biomedical $^{13}$C-magnetic resonance spectroscopy and imaging. AC may enhance in-vivo spectroscopy of slow metabolic processes, particularly in the brain, whereby $^{13}$C-labelled metabolites (e.g., amino acids) are produced. For such processes, hyperpolarization methods that produce very large signal gains which decay rapidly, are not useful. Furthermore, AC requires no additional equipment, while hyperpolarization requires a special and often costly apparatus. Another aspect of applying AC is to enhance the spins of a particular isotopomer, i.e. a metabolite with specific $^{13}$C-labelling, to provide spectral editing whereby the acquired signal of the specific labelling pattern is selectively enhanced.

We applied multiple rounds of AC using GRAPE and bypassed the Shannon bound on TCE in various ways. A single carbon was cooled by a factor of $4.61 \pm 0.02$, with $21.2 \pm 0.2$ information content, higher than $17.84$, the IC of the entire spin system at equilibrium. In a second experiment, the two carbons reached polarizations of $3.78 \pm 0.02$ and $3.40 \pm 0.02$, with an IC of $25.9 \pm 0.2$. Finally, in a third experiment, polarizations of $2.87 \pm 0.02$, $2.64 \pm 0.02$ for the carbons and $3.58 \pm 0.02$ for the proton were measured, to yield an IC of $28.0 \pm 0.2$.

The SIMPSON implementation of GRAPE allowed us to generate efficient and robust enough pulses to make the experiment possible. However, implementation of NMRQC algorithms using SIMPSON is still far from being easy. The parts missing from SIMPSON - the experimental limitations, as well as dephasing processes and numerical errors, cause a gap between the efficiency of the pulses as expected by the optimization and the observed efficiency (see section 3.6). We bypassed the problem by working with SIMPSON’s state to state mode that allowed shorter pulses, by increasing the robustness constraints, and by generating multiple pulses, selecting the ones with the best performance in the lab.

Possible future research directions are:

**Pulse design** - An alternative to SIMPSON is introduced in [50], an algorithm which generates smooth pulses, easier for the hardware to implement. Another alternative was recently introduced [21], an improved version of GRAPE which converges faster by utilizing a quasi-Newton method. This version (called BFGS-GRAPE) was implemented in Matlab within the Spinach package. The dephasing during the pulse transmission can be minimized by utilizing algorithms which take dephasing into account, or by giving higher priorities to trajectories of the density matrix with the least dephasing.

**Hardware** - The fidelity of the pulses can be improved by utilizing a feedback circuit [62] which reduces the fidelity degradation due to hardware bandwidth limitation.
**AC round optimization** - In the algorithm we implemented, we used the same pulses and the same delays in each round of AC. Tailoring specific pulses for each round may improve the final result. Using different delays in each round might also improve the result.

**$T_1$ relaxation model** - We observed that a spin’s thermalization time strongly depends on the polarization of adjacent spins, unlike the prediction of the independent-relaxation model. Adding a more accurate relaxation model may improve the predictions of the cooling factors obtainable by AC.
Appendices
Appendix A

Deriving the Free Hamiltonian in The Rotating Frame

It is easier to analyze the system when the coordinates of each spin in the density matrix are rotating by the same frequency of the RF field manipulating it. This way, the RF field will appear static (i.e., will not oscillate), simplifying the Liouville-von Neumann equation.

A.1 General Formula of the Rotating Frame

The evolution of the density matrix is determined by the Liouville-von Neumann equation:

\[ \dot{\rho}(t) = \frac{i}{\hbar} [\rho, H]. \] (A.1)

This equation can be written in the rotating frame. Defining \( \rho_r \) as the density matrix in the rotating frame:

\[ \rho(t) = e^{-i\omega t I_z} \rho_r(t) e^{i\omega t I_z}. \] (A.2)

Where \( \omega \) is the rotation frequency. The left hand side of equation A.1 can be written as:

\[ \dot{\rho}(t) = -i\omega I_z e^{-i\omega t I_z} \rho_r(t) e^{i\omega t I_z} + e^{-i\omega t I_z} \dot{\rho}_r(t) e^{i\omega t I_z} + i\omega e^{-i\omega t I_z} \rho_r(t) I_z e^{i\omega t I_z}. \] (A.3)

Since \( [e^{i\omega t I_z}, I_z] = 0 \),

\[ \dot{\rho}(t) = i\omega e^{-i\omega t I_z} [\rho_r(t), I_z] e^{i\omega t I_z} + e^{-i\omega t I_z} \dot{\rho}_r(t) e^{i\omega t I_z}. \] (A.4)

The right hand side of equation A.1 can also be expressed using \( \rho_r(t) \):
Defining $H_r = e^{i\omega t}I_z H e^{-i\omega t}I_z$:

$$i\frac{\hbar}{\hbar} [\rho(t), H] = i\frac{\hbar}{\hbar} e^{-i\omega t}I_z \rho_x(t) e^{i\omega t}I_z, H = i\frac{\hbar}{\hbar} e^{-i\omega t}I_z \rho_x(t) e^{i\omega t}I_z,$$

Substituting both sides in equation A.1:

$$i\omega e^{-i\omega t}I_z [\rho_x(t), I_z] e^{i\omega t}I_z + e^{-i\omega t}I_z \rho_x(t) e^{i\omega t}I_z = i\frac{\hbar}{\hbar} e^{-i\omega t}I_z \rho_x(t), H_r \right) e^{i\omega t}I_z.$$  \hspace{1cm} (A.5)

And so, the Liouville-von Neuman equation in the rotating frame is:

$$\rho_x(t) = i\frac{\hbar}{\hbar} \left[ \rho_x(t), H_r - \hbar\omega I_z \right].$$  \hspace{1cm} (A.6)

$H_r - \hbar\omega I_z$ is called the effective Hamiltonian.

### A.2 RF Term

On a typical NMR probe, the RF field is transmitted only along the x axis of the lab frame

$$H_{RF} = \hbar\gamma B_1 \cos(\omega t + \phi) \cdot I_x.$$  \hspace{1cm} (A.7)

Applying the rotating frame transformation:

$$e^{i\omega tI_z} \cdot \hbar\gamma B_1 \cos(\omega t + \phi) \cdot I_x \cdot e^{-i\omega tI_z} =$$

$$\hbar\gamma B_1 \left( e^{i\frac{\omega t}{2}} \right) \cdot \left( \cos(\omega t + \phi) \cdot \frac{1}{2} \right) \cdot \left( e^{-i\frac{\omega t}{2}} \right) \hspace{1cm} (A.11)$$

$$\hbar\gamma B_1 \left( e^{i(\omega t + \phi)} \cdot e^{-i\phi} \right) \hspace{1cm} (A.12)$$

$$\hbar\gamma B_1 \left[ (\cos(\phi) + \cos(2\omega t + \phi)) \cdot I_x + (\sin(\phi) - \sin(2\omega t + \phi)) \cdot I_y \right].$$  \hspace{1cm} (A.13)
Hence in the rotating frame, the RF field consists of two components, a static field, pointing at the angle $\phi$ in the XY plane, and a field rotating at the frequency $2\omega$. The fast rotating field has very little effect on the spin, and it is therefore neglected (the rotating wave approximation). Note that the angle $\phi$ is determined by the arbitrary decision of $t = 0$ compared to the pulse phase in the lab. Alternatively, we can say that the $x$ and $y$ axes of the rotating frame are determined by the NMR internal $\omega$ frequency generator. When transmitting at the same phase with the frequency generator, we are transmitting along the $x$ axis of the rotating frame. A 90° phase shift results in a transmission along the $y$ axis, etc.

In conclusion, given a lab Hamiltonian,

$$H = H_0 + H_{RF} = -\hbar \omega_L I_z + \hbar \gamma B_1 \cos(\omega t) I_x. \quad (A.15)$$

The effective Hamiltonian in the RF rotating frame is

$$H_{\text{eff}} = \hbar (\omega_L - \omega) I_z + \hbar \gamma B_1 \left( \cos(\phi) I_x + \sin(\phi) I_y \right). \quad (A.16)$$

The spin is on resonance when $\omega_L = \omega$. In that case the spin rotates around $B_1$ in the rotating frame (see Figure A.1). In the case $\omega_L \neq \omega$, the spin is off resonance, hence the effective magnetic field is the vector sum of $B_1$ and the remaining magnetic field at the $z$ direction $\omega L - \omega$. Note that if $|\omega - \omega_L| >> 1$, then $B_1$ is negligible, and the effective field points close to the $z$ axis. Hence transmitting far from resonance will not affect the spin.

### A.3 J-Coupling Term

Recall that the lab frame Hamiltonian (eq. 1.35) for two spins is:

$$H_0^{\text{lab}} = \hbar \omega_1 I_z^{(1)} + \hbar \omega_2 I_z^{(2)} + \hbar J_{12} I_z^{(1)} \cdot I_z^{(2)}. \quad (A.17)$$

In the case of homonuclear spins, both spins are controlled by the same RF field. Applying the transformation $H \to e^{i\omega t I_z^{(1)}} e^{i\omega t I_z^{(2)}} H e^{-i\omega t I_z^{(3)}} e^{-i\omega t I_z^{(1)}} - \hbar \omega I_z^{(1)} - \hbar \omega I_z^{(2)}$ on each of the spins with the same $\omega$ yields:
In the case of heteronuclear spins, each spin will be affected by an RF field with a different frequency. Since \( \Delta \omega \approx \Delta \Omega \) are close to the Larmor frequencies of the spins, and in a modern NMR and a typical molecule \( |\Omega_i - \Omega_j| \gg J_{ij} \), the oscillating terms rapidly average to zero, therefore:

\[
H_0 = h\delta_1 I_z^{(1)} + h\delta_2 I_z^{(2)} + hJ_{ij} I_z^{(1)} I_z^{(2)}.
\]  

(A.24)
From equations A.20 and A.24 we conclude that in the rotating frame:

\[ H_0 = \sum_i h\delta_i I_z^{(i)} + \sum_{ij \text{ homo.}} hJ_{ij} I^{(i)} \cdot I^{(j)} + \sum_{ij \text{ hetero.}} hJ_{ij} I_z^{(i)} I_z^{(j)}. \]  

(A.25)
Appendix B

NMR Spectrum Interpretation

While deriving the spectrum from a density matrix can be done using the Liouville-von Neumann equation, tomography, the inverse problem, requires several experiments as not all elements of the density matrix are visible in the spectrum. The spectrum of a spin 1/2 nucleus under a specific type of Hamiltonians is analyzed in this section.

B.1 Integral over the Spin’s Spectral Lines

As a private case, we’ll show that the integral over the real part of the spectrum $\hat{f}(\omega)$, is proportional to $\langle I_x \rangle$ at $t=0$.

\[
\text{Re} \int_{-\infty}^{\infty} d\omega \hat{f}(\omega) = \text{Re} \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} dt \cdot e^{-i\omega t} \cdot \text{tr} (\rho(t)I_+) . \tag{B.1}
\]

Reordering

\[
\text{Re} \int_{-\infty}^{\infty} dt \cdot \text{tr} (\rho(t)I_+) \cdot \int_{-\infty}^{\infty} d\omega e^{-i\omega t} . \tag{B.2}
\]

The integral over $\omega$ is the definition of the $\delta$ function

\[
\delta(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} d\omega . \tag{B.3}
\]

\[
2\pi \text{Re} \int_{-\infty}^{\infty} dt \cdot \text{tr} (\rho(t)I_+) \cdot \delta(t) = \tag{B.4}
\]

\[
= 2\pi \text{Re} (\text{tr} (\rho(0)I_+)) = 2\pi \text{tr} (\rho(0)I_x) = 2\pi \langle I_x (0) \rangle . \tag{B.5}
\]

Q.E.D

Hence the integral over the real part of the spectrum gives us the $I_x$ expectation value at time $t=0$. Similarly, the integral over the imaginary part of the spectrum is the expectation value of $I_y$ at $t=0$.  

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B.2 Spectrum Analysis

In this section we analyze the information on the density matrix extractable from a spectrum. We focus on Hamiltonians that are diagonal in the standard basis, and on a spectrum with distinct spectral lines (i.e., each line is identified with a unique energy transition). No dissipation is taken into account in the calculation as it has no effect on the results.

The spectrum has distinct spectral lines if the eigenvalues of the Hamiltonian, \( \{E_s\}_{s=0,2^n-1} \), satisfy for all \( i,j,k,l \):

\[
E_i - E_j = E_k - E_l \implies i = k, j = l.
\]  

An initial density matrix \( \rho(0) \) of \( n \) spin half nuclei can be written using the eigenstates of the Hamiltonian, namely, the standard basis:

\[
\rho(0) = \sum_{j,k=0}^{2^n-1} \alpha_{j,k} |j\rangle \langle k|.
\]  

The time evolution of the density matrix is:

\[
\rho(t) = e^{-\frac{iHt}{\hbar}}\rho(0)e^{\frac{iHt}{\hbar}} = \sum_{j,k=0}^{2^n-1} e^{-\omega_j - \omega_k} \alpha_{j,k} |j\rangle \langle k| = \sum_{j,k=0}^{2^n-1} e^{-i(\omega_j - \omega_k)t} \alpha_{j,k} |j\rangle \langle k|.
\]  

Here \( \omega_j = \frac{E_j}{\hbar} \). Without loss of generality, we focus on the spectral lines of the leftmost spin, and express the observable using the standard basis:

\[
I_+ \otimes 1_{2^n-1} = (I_x + iI_y) \otimes 1_{2^n-1} = \begin{pmatrix}
1 & \\
& \\
& & \\
& & \ddots & \\
& & & \\
& & & & \\
& & & & & 1
\end{pmatrix} = \sum_{l=0}^{2^n-1-1} |l\rangle \langle l + 2^n-1|.
\]  

Note that the last term expresses a state transition (flip) of the observed (leftmost) spin:

\[
|l\rangle \langle l + 2^n+1| = |l_0l_{n-2}l_{n-3} \ldots l_0\rangle \langle l_{n-2}l_{n-3} \ldots l_0|.
\]  

Here \( l_n \) is the \( n \)th bit of the binary representation of \( l \). The observed fid (without dissipation) is:

\[
f(t) = \text{tr}(I_+ \rho(t)) = \text{tr} \left( \sum_{j,k=0}^{2^n-1} \sum_{l=0}^{2^n-1-1} e^{-i(\omega_j - \omega_k)t} \alpha_{j,k} |j\rangle \langle k| \langle l + 2^n-1| \right)
\]

\[
f(t) = \sum_{l=0}^{2^n-1-1} \alpha_{l+2^n-1,l} e^{-i(\omega_{l+2^n-1} - \omega_l)t}.
\]  

Since the spectral lines are distinct, each line can be identified with a specific \( \alpha \), an element of the matrix \( \rho(0) \). Given a spectrum, we apply to each spectral line:

1. Find \( E_j \) and \( E_k \) matching the frequency of the line.

2. The integral over the line in the real spectrum equals the real part of \( \alpha_{j,k} \). The integral over the line in the imaginary spectrum equals the imaginary part of \( \alpha_{j,k} \).
The spectrum of each spin gives at most \(2^{n-1}\) spectral lines, translated to \(2^{n-1}\) elements of \(\rho(0)\). Therefore a full tomography of \(\rho(0)\) requires \(\Omega(2^n)\) spectra of spins.

For instance, if TCE were placed in an NMR spectrometer with higher magnetic field, the chemical shift between the carbons would be much larger than their mutual coupling, causing the effective Hamiltonian to become diagonal. In this scenario the four spectral lines of C2 are \(\omega_{C2} \pm J_{H,C2} \pm J_{C2,C1}/2\), correspond to the four entries \(\langle ij0| \rho |ij1\rangle\) for \(i,j \in \{0,1\}\); where the order of the spins in the Dirac notation is C1,C2,H.
Appendix C

SIMPSON Simulation of the Carbon Spectrum

The spectrum generated by the following program was utilized to determine the exact chemical shift between the two carbons in TCE. Their chemical shifts values in the simulation were changed until the spectral lines matched the spectrum received in the lab. output.fid and fft.spe are the fid and spectrum output of the program, readable by the program simplot, part of the SIMPSON package. The propagator, in this case the identity matrix, is written to the files real.txt and img.txt in a comma separated values (CSV) format.

#TCE: spectrum of C1 and C2

spinsys {
  # channels defines RF channels we can talk to
  channels 1H 13C
  # the actual nuclei in the system.
  nuclei 1H 13C 13C
  # chemical shift of spin #1 #2...
  # shift nuc, iso, aniso, eta, alpha, beta, gamma
  shift 2 -3.59p 0 0 0 0 0
  shift 3 +3.59p 0 0 0 0 0
  # jcoupling nuc1, nuc2, jiso, Janiso, eta(?), alpha, beta, gamma
  jcoupling 1 3 9 0 0 0 0 0
  jcoupling 1 2 200.8 0 0 0 0 0
  jcoupling 2 3 103.1 0 0 0 0 0
}

par {
  # set up liquid state
  method direct
  spin_rate 0
}
crystal_file alpha0beta0
gamma_angles 1
sw 3500
np 131072
# define initial density matrix
start_operator I2x + I3x
# detect_operator I2p+I3p
proton_frequency 600.55e6
}

# my procedure, writes a matrix to two files - real.txt and img.txt
proc writematrix {S} {

# saving real part of the matrix to the file "real.txt"
set f [open real.txt w]
for {set i 0} {\$i<[llength S]} {incr i} {
    for {set j 0} {\$j<[llength S]} {incr j} {
        puts -nonewline $f "[lindex[\$S\$i\$j]\$i\$j\0\]"
    }
    puts $f "\0"
}
close $f;

# saving imaginary part of the matrix to the file "img.txt"
set f [open img.txt w]
for {set i 0} {\$i<[llength S]} {incr i} {
    for {set j 0} {\$j<[llength S]} {incr j} {
        puts -nonewline $f "[lindex[\$S\$i\$j]\$i\$j\1\]"
    }
    puts $f "\1"
}
close $f
}

proc pulseq {} {
    global par

    reset
    # write pulse program here. none in this case.
    #...
    # get the propagator
    set U [matrix get propagator];
#write to files
writematrix $U

#acquisition
acq
set i 1;
for {set i 1} {$i < [expr $par(np)\]]} {incr i} {
    delay [expr 1e+6 /$par(sw)]
    acq
}
}

proc main {} {
    global par

    # calling the simulation procedure
    set output1 [fsimpson]

    # adding a "fake" relaxation by line broadening
    set lb [expr 10.0*$par(sw)/$par(np)]
    faddlb $output1 $lb 0
    fsave $output1 output.fid
    fft $output1
    fsave $output1 fft.spe

    free_all_shapes
}

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Appendix D

Hilbert Schmidt Inner Product as a Target Function

The state to state GRAPE algorithm finds the RF amplitudes and phases that evolve the initial density matrix \( \rho_0 \) to a desired density matrix \( \rho_{\text{desired}} \). In this section, we prove that the target function,

\[
\Phi = \text{tr} \left( \rho(T) \cdot \rho_{\text{desired}} \right)
\]  

has a unique maximum if \( \rho(T) \) equals \( \rho_{\text{desired}} \).

**Lemma:** For every unitary matrix \( U \) and density matrix \( \rho \),

\[
\max_U (\text{tr} \left( \rho U \rho U^\dagger \right)) = \text{tr} (\rho \rho).
\]  

Namely, the maximum is obtained for \( U = 1 \).

**Proof:** Hilbert-Schmidt inner product of two matrices is equivalent to the scalar product of the vectors created by spreading the elements of each matrix:

\[
\text{tr} (A^\dagger \cdot B) = \sum_{ij} a^\ast_{ij} b_{ij}.
\]  

Choosing one matrix to be \( \rho \) (hermitian), and the other to be \( U \rho U^\dagger \), we have

\[
\text{tr} (\rho^\dagger \cdot U \rho U^\dagger) = \text{tr} (\rho \cdot U \rho U^\dagger) = \sum_{ij} \rho_{ij} (U \rho U^\dagger)_{ij}.
\]  

Note that:

\[
\sum_{ij} |\rho_{ij}|^2 = \text{tr} (\rho \rho) = \text{tr} (U \rho U^\dagger \cdot U \rho U^\dagger) = \sum_{ij} |(U \rho U^\dagger)_{ij}|^2.
\]  

Hence, the vector forms of \( \rho \) and \( U \rho U^\dagger \) have equal L2-norm. To complete the proof, recall that the scalar product of two vectors with the same L2-norm is maximized if they are equal.

Returning to the target function, the evolution of density matrices is unitary, hence the precondition for \( \rho_{\text{desired}} \) is:
\[ \rho_{\text{desired}} = V \rho_0 V^\dagger = W \rho(T) W^\dagger \]  \hspace{1cm} (D.6)

for some unitary matrices \( V, W \). The target function therefore takes the form:

\[ \Phi = \text{tr} (\rho(T) \cdot \rho_{\text{desired}}) = \text{tr} (\rho(T) \cdot W \rho(T) W^\dagger) . \]  \hspace{1cm} (D.7)

From the lemma, we know that \( \Phi \) is maximized iff

\[ \rho(T) = W \rho(T) W^\dagger = \rho_{\text{desired}}. \]  \hspace{1cm} (D.8)

QED
Appendix E

Deriving an Analytical Expression for $\frac{\delta \Phi}{\delta u_k(j)}$

GRAPE maximizes the target function $\Phi$ by “walking” in the direction of the gradient. The analytic expression for the gradient is calculated by back propagation, a method that emerged from optimal control theory. The definition of the propagator $U_j$ (eq. 2.2) is:

$$ U_j = \exp \left\{ \frac{-i\Delta t}{\hbar} \left( H_0 + \sum_{k \in \{channel, axis\}} u_k(j) H_k \right) \right\}. \quad (E.1) $$

Assuming the Hamiltonian is constant during the time interval $\Delta t$, and $\|H \Delta t/\hbar\| \ll 1$, we note that the Hamiltonians $H_k$ becomes commutative to the first order of $\Delta t$. Hence,

$$ U_j \approx e^{-\frac{i\Delta t}{\hbar} u_k(j)H_k} \prod_{k \in \{channel, axis\}} e^{-\frac{i\Delta t}{\hbar} u_k(j)H_k}. \quad (E.2) $$

we can derive by a specific control variable $u_k(j)$:

$$ \frac{\delta U_j}{\delta u_k(j)} = -\frac{i\Delta t}{\hbar} \cdot H_k U_j. \quad (E.3) $$

The derivative of $U_j^\dagger$:

$$ 0 = \frac{\delta 1}{\delta u_k(j)} = \frac{\delta U_j^\dagger U_j}{\delta u_k(j)} = \frac{\delta U_j^\dagger}{\delta u_k(j)} U_j + U_j^\dagger \frac{\delta U_j}{\delta u_k(j)} = \frac{\delta U_j^\dagger}{\delta u_k(j)} U_j - \frac{i\Delta t}{\hbar} \cdot U_j^\dagger H_k U_j \quad (E.4) $$

hence:

$$ \frac{\delta U_j^\dagger}{\delta u_k(j)} U_j = \frac{i\Delta t}{\hbar} \cdot U_j^\dagger H_k U_j \quad (E.5) $$

$$ \frac{\delta U_j}{\delta u_k(j)} = \frac{i\Delta t}{\hbar} \cdot U_j^\dagger H_k. \quad (E.6) $$
The target function can be written as:

$$\Phi = \text{tr} \left( \lambda_j \rho_j \right) = \text{tr} \left( \lambda_j U_j \rho_{j-1} U_j^\dagger \right).$$  \hspace{1cm} (E.7)

Since $\lambda_j$ and $\rho_{j-1}$ are independent of $u_k(j)$,

$$\frac{\delta \Phi}{\delta u_k(j)} = \text{tr} \left( \lambda_j \frac{\delta U_j}{\delta u_k(j)} \rho_{j-1} U_j^\dagger + \lambda_j U_j \rho_{j-1} \frac{\delta U_j}{\delta u_k(j)} \right) = \frac{i \Delta t}{\hbar} \cdot \text{tr} \left( \lambda_j \left[ \rho_j, H_k \right] \right).$$  \hspace{1cm} (E.8)
Appendix F

Degrees of Freedom of the Polarization Exchange Unitary Transformation

In the design of a polarization exchange pulse we require that

- \( \text{start\_operator} \ 4I^z_{1} + I^z_{2} + I^z_{3} \propto \text{diag}(6, 4, 4, 2, -2, -4, -4, -6) \)
- \( \text{detect\_operator} \ I^z_{1} + 4I^z_{2} + I^z_{3} \propto \text{diag}(6, 4, -2, -4, 4, 2, -4, -6) \)

Note that the density matrices have two double degenerated eigenvalues: 4, -4. Hence the freedom is to choose how the subspace \(|001\rangle\), \(|010\rangle\) is mapped to the subspace \(|001\rangle\), \(|100\rangle\) and how the subspace \(|101\rangle\), \(|110\rangle\) is mapped to the subspace \(|001\rangle\), \(|110\rangle\). The general form of the unitary operation applied by the pulse is therefore:

\[
U = \begin{bmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \cos(\theta_1) e^{i\phi_1} & \sin(\theta_1) e^{i\phi_2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & \cos(\theta_2) e^{i\phi_5} & \sin(\theta_2) e^{i\phi_6} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \cos(\theta_1) e^{i(\phi_2 + \phi_3 - \phi_1)} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & e^{i\phi_2} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -\sin(\theta_2) e^{i\phi_7} & \cos(\theta_2) e^{i(\phi_6 + \phi_7 - \phi_5)} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & e^{i\phi_3}
\end{bmatrix}
\]  

Here \( \theta_1, \theta_2 \in \left[0, \frac{\pi}{2}\right] \). The pulse duration \(d\) and the interaction rates may constrain the parameters of \(U\). For example, if \(J_{\text{H}1\text{C}2}, J_{\text{H}2\text{C}1} \ll \frac{1}{d}\), then \(C_1\) (the least significant qubit) would be nearly isolated during the pulse. The transition from \(|001\rangle\) to \(|100\rangle\) while \(|000\rangle\) remains untouched requires an interaction between \(C_1\) and the rest of the molecule. As the pulse is short, and this transition requires long time due to

\[U_2 = \begin{pmatrix}
\cos(\theta)e^{i\phi_1} & \sin(\theta)e^{i\phi_2} \\
-\sin(\theta)e^{i\phi_3} & \cos(\theta)e^{i(\phi_2 + \phi_3 - \phi_1)}
\end{pmatrix}, \quad \theta \in \left[0, \frac{\pi}{2}\right].\]
to the small coupling, the corresponding matrix element $u_{5,2}$ would be negligible ($0 \leq \theta_1 \ll 1$), unlike the general form of equation F.1. Note that the pulse applies a SWAP gate in this scenario.

A general PE pulse will evolve each of the spins in the following way:

\[
U \cdot I_z^{(1)} \cdot U^\dagger = I_z^{(2)}
\]  

(F.2)

\[
U I_z^{(2)} U^\dagger = \left[ 1 - 1/2 \left( \cos(\theta_1) \right)^2 - 1/2 \left( \cos(\theta_2) \right)^2 \right] I_z^{(1)} + \left[ 1/2 \left( \cos(\theta_1) \right)^2 + 1/2 \left( \cos(\theta_2) \right)^2 \right] I_z^{(3)} + 
\]

\[
\left[ - (\cos(\theta_1))^2 + (\cos(\theta_2))^2 \right] \left[ I_z^{(2)} I_z^{(3)} - I_z^{(1)} I_z^{(2)} \right] + [ -1/2 \sin(2 \theta_1) \cos(-\phi_3 + \phi_1) - 1/2 \sin(2 \theta_2) \cos(-\phi_6 + \phi_4) \left[ I_x I_z^{(3)} + I_y I_y^{(3)} \right] + [-1/2 \sin(2 \theta_1) \sin(-\phi_3 + \phi_1) - 1/2 \sin(2 \theta_2) \sin(-\phi_6 + \phi_4) \left[ I_z I_x^{(3)} - I_y I_y^{(3)} \right] + [- \sin(2 \theta_1) \cos(-\phi_3 + \phi_1) + \sin(2 \theta_2) \cos(-\phi_6 + \phi_4) \left[ I_x I_z^{(3)} + I_y I_y^{(3)} \right] + [- \sin(2 \theta_1) \sin(-\phi_3 + \phi_1) + \sin(2 \theta_2) \sin(-\phi_6 + \phi_4) \left[ I_z I_x^{(3)} - I_y I_y^{(3)} \right]
\]  

(F.3)

\[
U I_z^{(3)} U^\dagger = \left[ 1 - 1/2 \left( \cos(\theta_1) \right)^2 - 1/2 \left( \cos(\theta_2) \right)^2 \right] I_z^{(1)} + \left[ 1/2 \left( \cos(\theta_1) \right)^2 + 1/2 \left( \cos(\theta_2) \right)^2 \right] I_z^{(3)} + 
\]

\[
\left[ - (\cos(\theta_1))^2 + (\cos(\theta_2))^2 \right] \left[ - I_z^{(2)} I_z^{(3)} + I_z^{(1)} I_z^{(2)} \right] + [ 1/2 \sin(2 \theta_1) \cos(-\phi_3 + \phi_1) + 1/2 \sin(2 \theta_2) \cos(-\phi_6 + \phi_4) \left[ I_x I_z^{(3)} + I_y I_y^{(3)} \right] + [-1/2 \sin(2 \theta_1) \sin(-\phi_3 + \phi_1) - 1/2 \sin(2 \theta_2) \sin(-\phi_6 + \phi_4) \left[ - I_x I_z^{(3)} + I_y I_y^{(3)} \right] + [\sin(2 \theta_1) \cos(-\phi_3 + \phi_1) - \sin(2 \theta_2) \cos(-\phi_6 + \phi_4) \left[ I_x I_z^{(3)} + I_y I_y^{(3)} \right] + [- \sin(2 \theta_1) \sin(-\phi_3 + \phi_1) + \sin(2 \theta_2) \sin(-\phi_6 + \phi_4) \left[ - I_x I_z^{(3)} + I_y I_y^{(3)} \right]
\]  

(F.4)

We see that the polarization on H is transferred only to C2 and the other spins are transferred to various coherences. However summing the last two equations results in a simple expression:

\[
U \left( I_z^{(2)} + I_z^{(3)} \right) U^\dagger = I_z^{(1)} + I_z^{(3)}.
\]  

(F.5)
Appendix G

Source Code Examples for SIMPSON Running Optimal Control

This example program generates a pulse that swaps the polarization of the hydrogen and C2. The pulse is robust to RF inhomogeneity of ±15%.

G.1 Input File

spinsys {

    # channels defines RF channels we can talk to
    channels 1H 13C

    # the actual nuclei in the system.
    nuclei 1H 13C 13C

    # chemical shift:
    # syntax: shift nuc, iso, aniso, eta, alpha, beta, gamma
    # units are in hz, unless postfix p is added to the number which
    # sets the units to ppm.
    shift 2 -3.59p 0 0 0 0
    shift 3 +3.59p 0 0 0 0

    # jcoupling nuc1, nuc2, jiso, Janiso, eta, alpha, beta, gamma
    jcoupling 1 3 8.9 0 0 0 0
    jcoupling 1 2 200.752 0 0 0 0
    jcoupling 2 3 103.1 0 0 0 0

}

Note that the spins are enumerated by the order they are defined: 1-H, 2-C2, 3-C1.

par {

}
# set up liquid state mode
spin_rate 0
crystal_file alpha0beta0
gamma_angles 1

# initial density matrix
start_operator 4*I1z+I2z+I3z

# desired density matrix
detect_operator I1z+4*I2z+I3z

# RF inhomogeneity profile file
rfprof_file rf_file2d15%

# duration of the shaped pulse (in microsec)
variable duration 6e+3

# number of elements in the shape
variable NOC 5000

# NMR primary magnetic field strength
proton_frequency 500.133e+6

# limit to the number of iterations in oc_optimize
oc_max_iter 500

# must be defined in optimal control mode
conjugate_fid false
}

proc pulseq {} {
# makes par structure visible to this procedure, as well
# as the structures that keeps the rf shape: rfsh1,rfsh2.
global par rfsh1 rfsh2

# reset propagator
reset

# apply a shaped pulse
pulse_shaped $par(duration) $rfsh1 $rfsh2

# Optimal control related command which calculates either target
# function or gradients (depending what calls the pulse sequence).
oc_acq_hermit
}

proc gradient {} {
    global par rfsh1 rfsh2

    # prepares for the call for fsimpson which would calculate

88
# the gradient. par(np) sets the number of
# data elements fsimpson would output. since the gradient
# is of 2 channels, and the pulse has NOC points, the number
# of data elements in the gradient would be 2*NOC.
set par(np) [expr $par(NOC)*2]

# call fsimpson to calculate the gradient.
set f [fsimpson]

return $f
}

proc target_function {} {
    global par rfsh1 rfsh2

    # same as in gradient. target function is a scalar
    # so setting par(np) to be 1.
    set par(np) 1

    # calls fsimpson to evaluate the target function
    set temp [fsimpson]

    # extract the target function from the structure returned
    # by fsimpson
    set f [expr $f+[findex $temp 1 -re]]

    return [format "%.20f" $f]
}

proc main {} {
    global par rfsh1 rfsh2

    # generate initial pulse sequences randomly:
    # a random shape with less points is created, and then interpolated
    # to the desired number of points in the pulse.

    set rfsh1 [rand_shape 2000 $par(NOC) 30]
    set rfsh2 [rand_shape 2000 $par(NOC) 30]

    # do optimization by modifying rfsh1 rfsh2
    set tfopt [oc_optimize $rfsh2 $rfsh1]

    # save results
    save_shape $rfsh1 $par(name)\_sol_H.dat
G.2 Robustness to Parameters

In this code section, robustness to NMR primary magnetic field is demonstrated by modifying target_function and gradient.

```tcl
proc gradient {} {
    global par rfsh1 rfsh2
    set par(np) [expr $par(NOC)*2]
    set first 1
    # saves copy of the value of proton_frequency
    set temp $par(proton_frequency)
    # this loop calculates the gradient in various values
    # of proton_frequency
    for { set B -150 } { $B<=150 } { set B [expr $B+50] } {
        if { $first==0 } {
            set par(proton_frequency) [expr $B+$temp]
        } else {
            set f [fsimpson]
            set first 0
            set g [fsimpson]
            fadd $f $g
            funload $g
        }
    }
    # restore proton_frequency to its nominal value.
```

90
set par(proton_frequency) $temp

# return the sum of all gradients.
return $f
}

proc target_function {} {
    global par rfsh1 rfsh2
    set par(np) 1
    set f 0
    set saved $par(proton_frequency)
    for { set B -150 } { $B<=150 } { set B [expr $B+50] } {
        set par(proton_frequency) [expr $saved + $B]
        # evaluates the target function in current magnetic field
        set temp [fsimpson]
        # add the result to previous ones stored in f.
        set f [expr $f+[findex $temp 1 -re]]
    }
    # restore proton_frequency to its nominal value
    set par(proton_frequency) $saved
    return [format "%.20f" $f]
}

G.3 RF Inhomogeneity File

The RF inhomogeneity file is a text file with an extension rf (e.g., rf_file2d15%.rf). The file has the following structure: First line: <number of elements in the profile> <number of channels>, while all subsequent lines contain <RF scaling factor for 1st channel> <same for 2nd channel>... <weight factor> (for RF scaling factors, 1.0 designates nominal RF field strength).

13 2
1 1 1
1.1 0.9 1
1.1 1.1 1
0.9 0.9 1
0.9 1.1 1
1.15 1.15 1
1.15 0.85 1
0.85 1.15 1
0.85 0.85 1
1.15 1 1
Appendix H

Unitary Tables Examples

It is possible to use a table instead of a matrix to describe a unitary operator, so that its effect on different product operators is easier to see. In each row of the table, the unitary operator is applied on a different product operator and the projection of the resulted density matrix on each product operator is written on the columns. For example, the following table represent the unitary operation $\sigma_x$, a $180^\circ$ rotation around the x axis:

$$
\begin{array}{c|ccc}
 & I_x & I_y & I_z \\
\hline
\sigma_x I_x \sigma_x^\dagger &=& 1 \\
\sigma_x I_y \sigma_x^\dagger &=& -1 \\
\sigma_x I_z \sigma_x^\dagger &=& -1 \\
\end{array}
$$

Table H.1: The unitary operation $\sigma_x$ in a table representation.

Explicitly,

$$
\begin{align*}
\sigma_x I_x \sigma_x^\dagger &= I_x \\
\sigma_x I_y \sigma_x^\dagger &= -I_y \\
\sigma_x I_z \sigma_x^\dagger &= -I_z.
\end{align*}
$$

(H.1) (H.2) (H.3)

Note that $I_x$ is unaffected, while $I_y$ and $I_z$ are inverted. In this representation, a $2^n \times 2^n$ unitary matrix will translate to a $(4^n - 1) \times (4^n - 1)$ table. In AC, the off diagonal product operators vanish during the wait periods, hence the table representation becomes compact and useful. For example, the following table shows only the diagonal product operators of a SWAP gate on two spin system:

$$
\begin{array}{c|ccc}
 & I_z & S_z & I_z S_z \\
\hline
U_{\text{swap}} I_z U_{\text{swap}}^\dagger &=& 1 \\
U_{\text{swap}} S_z U_{\text{swap}}^\dagger &=& 1 \\
U_{\text{swap}} I_z S_z U_{\text{swap}}^\dagger &=& 1 \\
\end{array}
$$

Table H.2: A table representation of a SWAP gate applied on two spin system.
Appendix I

Bruker Pulse Program

The standard pulse program \texttt{selzg} was used for calibrating the carbon power level of shaped pulses. The following pulse program was used for 7 rounds of AC, maximizing the polarization on C1:

\begin{verbatim}
;L1 rounds of AC + 90
;1D sequence
;
;CLASS=HighRes
;$DIM=1D
;$TYPE=
;$SUBTYPE=
;$COMMENT=

#include <Avance.incl>

1 ze
2 30m
d1

;;;;;;;main loop
start, d3

(p13:sp1 ph1):f1  (p13:sp2 ph1):f2  ; polarization exchange
 .5m
d2

(p14:sp3 ph1):f1  (p14:sp4 ph1):f2  ; compression
 .5m

lo to start times l1

;;;;;;;end of main loop

;;;;;;;end of main loop
d4

(p15:sp5 ph1):f1  (p15:sp6 ph1):f2  ; shaped "90" pulse

d5
go=2 ph31
30m mc #0 to 2 F0(zd)

exit

ph1=0
\end{verbatim}
\texttt{ph31=0}

;\texttt{d1 : relaxation delay}
;\texttt{d2 : delay before pulse \#2}
;\texttt{d3 : delay before pulse \#1}
;\texttt{d4 : delay before pulse \#3 measurement}

;\texttt{p13 : time usec of the first pulse}
;\texttt{sp1 : carbon shaped pulse \#1 power [db]}
;\texttt{sp2 : hydrogen shaped pulse \#1 power [db]}

;\texttt{p14 : time usec of the second pulse}
;\texttt{sp3 : carbon shaped pulse \#2 power [db]}
;\texttt{sp4 : hydrogen shaped pulse \#2 power [db]}

;\texttt{p15 : time usec of the third pulse}
;\texttt{sp5 : carbon shaped pulse \#3 power [db]}
;\texttt{sp6 : hydrogen shaped pulse \#3 power [db]}

;\texttt{l1 : loop counter}
Appendix J

Cross Relaxation Observations

The main source of thermalization is the spins energy transitions caused by fluctuations in the magnetic field [45]. The thermal motion of the molecules changes the distance-dependent interactions which usually are not observable in the spectrum of liquid state NMR. Quadrupole, dipole-dipole and anisotropic chemical shift interactions are the main sources of the fluctuations. Throughout this work we assumed \( T_1 \) relaxation of a spin is independent of the states of other spins:

\[
\frac{d\langle I_z \rangle}{dt} = -\frac{1}{T_1} (\langle I_z \rangle - \langle I_{z,eq} \rangle).
\]  

(J.1)

Here \( \langle I_z \rangle \) is the temporal polarization of the spin, and \( \langle I_{z,eq} \rangle \) is the equilibrium polarization. Lab observation suggested that this model is not accurate, and we assume that the cross relaxation process dominates the relaxation in the presence of cooled spins. Solomon equations [70] describe the cross relaxation model for two spins, I and S:

\[
\frac{d\langle I_z \rangle}{dt} = -\frac{1}{T_1^I} (\langle I_z \rangle - \langle I_{z,eq} \rangle) - \frac{1}{K_{1,2}} (\langle S_z \rangle - \langle S_{z,eq} \rangle)
\]

\[
\frac{d\langle S_z \rangle}{dt} = -\frac{1}{T_1^S} (\langle S_z \rangle - \langle S_{z,eq} \rangle) - \frac{1}{K_{1,2}} (\langle I_z \rangle - \langle I_{z,eq} \rangle).
\]  

(J.2)

Here \( \frac{1}{K_{1,2}} \) is the cross relaxation rate constant, and \( \frac{1}{T_1} \) is the auto relaxation rate constant of the spin. Instead of a single exponential, the solution is now a sum of two exponents. Table J.1 shows the measured the polarization of C1 and C2 after multi round AC, followed by a delay D4.\(^1\)

\(^1\)D4\(>1\) msec due to hardware limitations.
<table>
<thead>
<tr>
<th>D4</th>
<th>C1</th>
<th>C2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1msec</td>
<td>4.61</td>
<td>1.77</td>
</tr>
<tr>
<td>1s</td>
<td>4.38</td>
<td>1.77</td>
</tr>
<tr>
<td>2s</td>
<td>4.23</td>
<td>1.79</td>
</tr>
<tr>
<td>3s</td>
<td>4.11</td>
<td>1.8</td>
</tr>
<tr>
<td>4s</td>
<td>3.97</td>
<td>1.78</td>
</tr>
<tr>
<td>5s</td>
<td>3.86</td>
<td>1.74</td>
</tr>
<tr>
<td>6s</td>
<td>3.76</td>
<td>1.77</td>
</tr>
<tr>
<td>7s</td>
<td>3.64</td>
<td>1.73</td>
</tr>
<tr>
<td>8s</td>
<td>3.55</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table J.1: Measured polarization of C1 and C2 after AC with a D4 delay.

Note that C2 retain its polarization for more than 8 seconds though its measured T$_1$ is 17.3s. The effective T$_1$ of C1 in this process is 23s, calculated by fitting the polarization to a decaying exponent, while the measured T$_1$ is 29.2s. Although the polarization retention of C2 can be explained by a negative $K_{1,2}$, the cross relaxation term should have slowed the thermalization of C1 as well. A possible explanation is that T$_1$ values should have been measured differently, taking cross relaxation into account. Alternatively, the Solomon equations might be insufficient to describe all the processes in TCE, and a better model is required.
Appendix K

Thermalization of Linear and Trilinear Product Operators in a 3-Spin System

We explore the thermalization of a 3-spin system with an initial polarizations $\alpha_1, \alpha_2, \alpha_3$ and with a trilinear term:

$$\rho(0) = \frac{1}{8} + \frac{\alpha_1}{8} \sigma_1^z + \frac{\alpha_2}{8} \sigma_2^z + \frac{\alpha_3}{8} \sigma_3^z + \frac{\eta}{8} \sigma_1^z \sigma_2^z \sigma_3^z. \tag{K.1}$$

Here $\sigma_1^z = \mathbb{1}_4 \otimes \sigma_z$, $\sigma_2^z = \mathbb{1}_2 \otimes \sigma_z \otimes \mathbb{1}_2$ and $\sigma_3^z = \mathbb{1}_4 \otimes \sigma_z$. Explicitly $\rho(0)$ is:

$$\rho(0) = \frac{1}{8} \text{diag}(1 + \alpha_1 + \alpha_2 + \alpha_3 + \eta, 1 + \alpha_1 + \alpha_2 - \alpha_3 - \eta, 1 + \alpha_1 - \alpha_2 + \alpha_3 - \eta, 1 + \alpha_1 - \alpha_2 - \alpha_3 + \eta, 1 - \alpha_1 + \alpha_2 + \alpha_3 - \eta, 1 - \alpha_1 + \alpha_2 - \alpha_3 + \eta, 1 - \alpha_1 - \alpha_2 + \alpha_3 + \eta, 1 - \alpha_1 - \alpha_2 - \alpha_3 - \eta). \tag{K.2}$$

The first entry in the diagonal is the probability to find the system in the state $|000\rangle$, the second entry is the probability to find the system in the state $|001\rangle$ etc. In a state expressed by a tensor product we can let each spin thermalize independently (in this model we ignore cross relaxation). If the $j^{th}$ spin starts in the state $|0\rangle$ and relaxes to the equilibrium polarization $\varepsilon_j$, the evolution of its density matrix is:

$$\rho_{0 \to \text{eq}}(t) = e^{-\frac{t}{\tau_1}} |0\rangle \langle 0| + \left(1 - e^{-\frac{t}{\tau_1}}\right) \left(\frac{\mathbb{1}_2 + \varepsilon_j \sigma_z}{2}\right) = e^{-\frac{t}{\tau_1}} \left(\frac{\mathbb{1}_2 + \sigma_z}{2}\right) + \left(1 - e^{-\frac{t}{\tau_1}}\right) \left(\frac{\mathbb{1}_2 + \varepsilon_j \sigma_z}{2}\right). \tag{K.3}$$
Rearranging:

$$\rho_{0 \rightarrow eq}^j(t) = \frac{1}{2} + e^{-\frac{t}{T_j}} \sigma_z \varepsilon_j \left(1 - e^{-\frac{t}{T_j}}\right) \sigma_z.$$

Similarly, the thermalization the jth spin from the state $|1\rangle$ to equilibrium is

$$\rho_{1 \rightarrow eq}^j(t) = \frac{1}{2} - e^{-\frac{t}{T_j}} \sigma_z \varepsilon_j \left(1 - e^{-\frac{t}{T_j}}\right) \sigma_z.$$ (K.5)

By defining

$$f_0(t, j) = e^{-\frac{t}{T_j}} \varepsilon_j \left(1 - e^{-\frac{t}{T_j}}\right),$$

$$f_1(t, j) = -e^{-\frac{t}{T_j}} \varepsilon_j \left(1 - e^{-\frac{t}{T_j}}\right),$$

$$\rho_{0 \rightarrow eq}^j(t)$$ and $$\rho_{1 \rightarrow eq}^j(t)$$ becomes

$$\rho_{0 \rightarrow eq}^j(t) = \frac{1}{2} + f_0(t, j) \sigma_z,$$

$$\rho_{1 \rightarrow eq}^j(t) = \frac{1}{2} + f_1(t, j) \sigma_z.$$ (K.7)

The thermalization of pure states can be written using the last pair of equations. For instance, the thermalization of $|011\rangle$ is

$$\rho_{0 \rightarrow eq}^1(t) \otimes \rho_{1 \rightarrow eq}^2(t) \otimes \rho_{1 \rightarrow eq}^3(t).$$ (K.8)

Now we return to equation K.2, and write it as a mixture of pure states:

$$\rho(0) = \sum_{k,l,m \in \{0,1\}} \left(1 + (-1)^k \alpha_1 + (-1)^l \alpha_2 + (-1)^m \alpha_3 + (-1)^{k+l+m} \eta \right) |klm\rangle \langle klm|.$$ (K.9)

We know how each pure state thermalizes:

$$\rho(t) = \sum_{k,l,m \in \{0,1\}} \left(1 + (-1)^k \alpha_1 + (-1)^l \alpha_2 + (-1)^m \alpha_3 + (-1)^{k+l+m} \eta \right) \rho_{k \rightarrow eq}^1(t) \otimes \rho_{l \rightarrow eq}^2(t) \otimes \rho_{m \rightarrow eq}^3(t).$$ (K.10)

By substituting the thermalization terms, equation K.10 becomes:

$$\rho(t) = \sum_{k,l,m \in \{0,1\}} \left(1 + (-1)^k \alpha_1 + (-1)^l \alpha_2 + (-1)^m \alpha_3 + (-1)^{k+l+m} \eta \right) \frac{1}{64} \left(\mathbb{I} + f_k(t, 1) \sigma_z^1 \right) \left(\mathbb{I} + f_l(t, 2) \sigma_z^2 \right) \left(\mathbb{I} + f_m(t, 3) \sigma_z^3 \right).$$ (K.11)

Grouping the product operators, we notice that the coefficient of $\mathbb{I}$ is

$$\frac{1}{64} \sum_{k,l,m \in \{0,1\}} \left(1 + (-1)^k \alpha_1 + (-1)^l \alpha_2 + (-1)^m \alpha_3 + (-1)^{k+l+m} \eta \right) = \frac{1}{8},$$ (K.12)
as expected. The coefficient of $\sigma_1^1$ is

$$
\frac{1}{64} \sum_{k,l,m \in \{0,1\}} (1 + (-1)^k \alpha_1 + (-1)^l \alpha_2 + (-1)^m \alpha_3 + (-1)^{k+l+m+\eta}) f_k(t, 1) = \tag{K.13}
$$

$$
\frac{1}{64} \sum_{k \in \{0,1\}} (4 + 4(-1)^k \alpha_1) f_k(t, 1) = \frac{1}{16} (f_0(t, 1) + f_1(t, 1)) + \frac{\alpha_1}{16} (f_0(t, 1) - f_1(t, 1)). \tag{K.14}
$$

We will make extensive use of the next equation pair to simplify expressions:

$$
f_0(t, 1) + f_1(t, 1) = 2\varepsilon_1 \left(1 - e^{-\frac{t}{T}}\right) \tag{K.15}
$$

$$
f_0(t, 1) - f_1(t, 1) = 2e^{-\frac{t}{T}}. \tag{K.16}
$$

The $\sigma_1^1$ coefficient is therefore:

$$
\frac{1}{8} \varepsilon_1 \left(1 - e^{-\frac{t}{T}}\right) + \frac{\alpha_1}{8} e^{-\frac{t}{T}}. \tag{K.16}
$$

To verify the result: on $t = 0$ the coefficient is $\frac{\alpha_1}{8}$; at $t = \infty$ the coefficient is $\frac{\alpha_1}{8}$ – namely, a polarization of $\varepsilon_1$. From symmetry, the same applies to the coefficients of $\sigma_2^1$ and $\sigma_3^1$.

We now examine the coefficient of bilinear term $\sigma_1^2\sigma_2^1$:

$$
\frac{1}{64} \sum_{k,l,m \in \{0,1\}} (1 + (-1)^k \alpha_1 + (-1)^l \alpha_2 + (-1)^m \alpha_3 + (-1)^{k+l+m+\eta}) f_k(t, 1)f_l(t, 2) = \tag{K.17}
$$

$$
\frac{1}{32} \sum_{k,l \in \{0,1\}} (1 + (-1)^k \alpha_1 + (-1)^l \alpha_2) f_k(t, 1)f_l(t, 2) = \tag{K.18}
$$

$$
\frac{1}{32} [f_0(t, 1)f_0(t, 2) + f_0(t, 1)f_1(t, 2) + f_1(t, 1)f_0(t, 2) + f_1(t, 1)f_1(t, 2)] + \tag{K.19}
$$

$$
\frac{\alpha_1}{32} [f_0(t, 1)f_0(t, 2) + f_0(t, 1)f_1(t, 2) - f_1(t, 1)f_0(t, 2) - f_1(t, 1)f_1(t, 2)] +
$$

$$
\frac{\alpha_2}{32} [f_0(t, 1)f_0(t, 2) - f_0(t, 1)f_1(t, 2) + f_1(t, 1)f_0(t, 2) - f_1(t, 1)f_1(t, 2)].
$$

Rearranging:

$$
\frac{1}{32} [f_0(t, 1)(f_0(t, 2) + f_1(t, 2)) + f_1(t, 1)(f_0(t, 2) + f_1(t, 2))] + \tag{K.20}
$$

$$
\frac{\alpha_1}{32} [f_0(t, 1)(f_0(t, 2) + f_1(t, 2)) - f_1(t, 1)(f_0(t, 2) + f_1(t, 2))] +
$$

$$
\frac{\alpha_2}{32} [f_0(t, 1)(f_0(t, 2) - f_1(t, 2)) + f_1(t, 1)(f_0(t, 2) - f_1(t, 2))].
$$
\[
\frac{1}{32} \left\{ f_0(t, 1) \left[ 2\varepsilon_2 \left( 1 - e^{-\frac{1}{T^2}} \right) \right] + f_1(t, 1) \left[ 2\varepsilon_2 \left( 1 - e^{-\frac{1}{T^2}} \right) \right] \right\} + \\
\frac{\alpha_1}{32} \left\{ f_0(t, 1) \left[ 2\varepsilon_2 \left( 1 - e^{-\frac{1}{T^2}} \right) \right] - f_1(t, 1) \left[ 2\varepsilon_2 \left( 1 - e^{-\frac{1}{T^2}} \right) \right] \right\} + \\
\frac{\alpha_2}{32} \left[ f_0(t, 1) \left( 2e^{-\frac{1}{T^2}} \right) + f_1(t, 1) \left( 2e^{-\frac{1}{T^2}} \right) \right] = \\
\frac{1}{32} \left[ 2\varepsilon_2 \left( 1 - e^{-\frac{1}{T^2}} \right) \right] \left[ 2\varepsilon_1 \left( 1 - e^{-\frac{1}{T^2}} \right) \right] + \\
\frac{\alpha_1}{32} \left\{ f_0(t, 1) \left[ 2\varepsilon_2 \left( 1 - e^{-\frac{1}{T^2}} \right) \right] - f_1(t, 1) \left[ 2\varepsilon_2 \left( 1 - e^{-\frac{1}{T^2}} \right) \right] \right\} + \\
\frac{\alpha_2}{32} \left[ f_0(t, 1) \left( 2e^{-\frac{1}{T^2}} \right) + f_1(t, 1) \left( 2e^{-\frac{1}{T^2}} \right) \right] = \tag{K.21}
\]

Assuming \( \alpha_1, \alpha_2, \alpha_3, \varepsilon_j \ll 1 \), we approximate to the first order of these small variables, and hence the entire \( \sigma_1^x \sigma_2^z \) coefficient as well as all other bilinear terms are neglectable.

The coefficient of the trilinear term is:

\[
\frac{1}{64} \sum_{k,l,m \in \{0,1\}} \left( 1 + (-1)^k \alpha_1 + (-1)^l \alpha_2 + (-1)^m \alpha_3 + (-1)^{k+l+m} \eta \right) f_k(t, 1) f_l(t, 2) f_m(t, 3). \tag{K.23}
\]

We’ll deal with each part separately:

\[
\frac{1}{64} \sum_{k,l,m \in \{0,1\}} f_k(t, 1) f_l(t, 2) f_m(t, 3) = \tag{K.24}
\]

\[
= \frac{1}{64} \left( f_0(t, 1) + f_1(t, 1) \right) \left( f_0(t, 2) + f_1(t, 2) \right) \left( f_0(t, 3) + f_1(t, 3) \right) = O(\varepsilon_1 \varepsilon_2 \varepsilon_3). \tag{K.25}
\]

The \( \alpha_1 \) coefficient is:

\[
= \frac{1}{64} \left( f_0(t, 1) - f_1(t, 1) \right) \left( f_0(t, 2) + f_1(t, 2) \right) \left( f_0(t, 3) + f_1(t, 3) \right) = O(\varepsilon_2 \varepsilon_3). \tag{K.26}
\]

The coefficients for \( \alpha_2 \) and \( \alpha_3 \) are similarly neglected. Hence we are only left with the \( \eta \) term:

\[
= \frac{1}{64} \left( f_0(t, 1) - f_1(t, 1) \right) \left( f_0(t, 2) - f_1(t, 2) \right) \left( f_0(t, 3) - f_1(t, 3) \right) = \frac{1}{8} e^{-\frac{1}{T^2}} - \frac{1}{T^2} - \frac{1}{T^2}. \tag{K.27}
\]

In conclusion, the evolution of the density matrix from the initial state, in a small polarizations
regime, is given by

\[
\rho(t) = \sum_{j=1,2,3} \left[ \frac{1}{8} \varepsilon_j \left( 1 - e^{-\frac{t}{T_1^j}} \right) + \frac{\alpha_j}{8} e^{-\frac{t}{T_1^j}} \right] \sigma_z^j + \frac{\eta}{8} e^{-\frac{t}{T_1^j}} - \frac{\eta}{T_2^j} - \frac{\eta}{T_3^j} \sigma_z^j \sigma_z^2 \sigma_z^3.
\] (K.28)

Each of the product operators relaxes independently of the others. The linear terms relax by the appropriate \( T_1 \) value to their equilibrium polarization, and the trilinear term relaxes to zero with a time constant \( \tau \):

\[
\frac{1}{\tau} = \sum_{j=1,2,3} \frac{1}{T_1^j}.
\] (K.29)
Bibliography


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בעזרת כלים של דחיסה מידע או source coding, ניתן להקטין את מידת האקראיות (להגדיל את הקיטוב) של ספינים מסוימים על ידי פעולות אוניטריות, כגון בקרה מיטבית. כך שפונקציית הפולסים שמשתמשת בתהליך פולסים עמידים יותר לפרמטרים הבעייתיים, היא הפיכה של תהליך בר סופיים של תחומי מתורת האופטימיזציה המוצא את הדרך להפעלת בקרה של מערכת לאורך זמן.

מטרות העברת דחיסה בדמת pracę במעבדה, כמו גם במעבדות חומרים של חומצה אמינית קוררו באופן דומה. דחיסה במד 하는uchen, בשני פחمي, שהמערכת הגיעה למחזור יציב ביחס למטרת עבודה זו היא לבצע מספר מחזורים של קירור אלגוריתמי. למעבדה שהדחיסה מתבצעת במערכת סגורה, יאבדו החום העודף לסביבה בזמן שספיני החישוב עדיין קרים. החום העודף לסביבה בזמן שספיני החישוב עדיין קרים, יוחלו לתשלום על גביש של חומצה אמינית קוררו באופן דומה במד, באמצעות אמבט חום מעבר לחסם שנון לוורוד למחזור קבוע.

ל堕ור הדרושים לקירור האלגוריתמי, דחיסה במד, מתבצעת במערכת סגורה. במילים אחרות, במד, המחשב מתבצע על פחמן בקיטוב זה, הטמפרטורה האפקטיבית של הפחמן בקיטוב זה היא 2 מעלות קלווין.

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Quantum computers are quantum systems that, with the help of phenomena such as superposition and entanglement, allow for performing computations more efficiently than classical computers. Dynamic nuclear polarization, para hydrogen, and cooling are techniques used in the research. The cooling algorithm involves the transfer of polarization between nuclei, and the cooling algorithm, which is a research topic, is used in the work. Dynamic nuclear polarization is commonly used in chemical analysis and the identification of chemical and biological processes. Para hydrogen is another technique used in the work. Dynamic nuclear polarization is a technique that allows for the efficient solution of problems and the analysis of complex chemical and biological processes. The work demonstrates that quantum computers can provide exponential speedup over classical computers, which is a remarkable improvement in the field of computer science.
The research was supervised by Professor/Dr. Tal Moran in the Faculty of Computer Science.

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בקרת מיטבית

燊ור על 먹קר

לשם مليוי חלקי של הדרישות ללא להישאר לקבילה החודר המגיסטר
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