

Analytic Theory of Polarization Transfer in Multi-spin Systems

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of BS-MS dual degree in Science*



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“If you want to shine like a sun .First burn like a sun”

Dr. A.P.J. Abdul Kalam

“If you can Dream it, you can do it.”

Marie Curie

*Dedicated to the Missile man of India,
Dr.A.P.J. Abdul Kalam, the man who told us
to Dream High and to the precious gifts of my
life who encouraged me to follow my Dreams*

Certificate of Examination

This is to certify that the dissertation titled "**Analytic theory of Polarization Transfer in multi-spin systems**" submitted by Ms. **Lakshmi Bhai N V** (Reg. No. MS11064) for the partial fulfilment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

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Dated: April 22,2016

Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr.Ramesh Ramachandran at the Indian Institute of Science Education and Research Mohali.

This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Lakshmi Bhai N V
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Dated: April 22,2016

In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr.Ramesh Ramachandran
(Supervisor)

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Abbreviations

BCH formula	Baker-Campbell-Hausdorff formula
CS	Chemical Shift
CSA	Chemical Shift Anisotropy
CP experiment	Cross Polarization Experiment
DQ	Double Quantum
HORROR Experiment	Homonuclear Rotary Resonance
NMR	Nuclear Magnetic Resonance
QL Theorem	Quantum Liouville Theorem
ZQ	Zero Quantum

Abstract

by Lakshmi Bhai N V

Understanding the mechanism of polarization transfer in NMR spectroscopy is an active area of research both from an experimental as well as theoretical perspective. In this regard, an analytic theory based on the reduced density matrix formalism is proposed to develop models for quantifying the polarization transfer among spins in the solid-state. We believe that the analytic results could be quite handful in quantifying the polarization transfer in band-selective and relayed polarization experiments in solid-state NMR.

Chapter 1

Introduction

The phenomenon of nuclear magnetic resonance (NMR) arises from a quantum property called 'spin'. Being a quantum mechanical property, the spin of a nucleus is characterized through a label, I (commonly referred to as a spin quantum number). In NMR spectroscopy, each nucleus with a given spin quantum number is characterized through the presence of $2I+1$ spin states and is detected through spectroscopy by inducing transitions between the nuclear spin states. To induce appreciable transitions between the nuclear spin states, intense static magnetic fields are applied to lift the degeneracy of the nuclear spin states. Subsequently, employing oscillating magnetic fields, transitions are induced between the nuclear spin states through a resonance matching between the frequency of the oscillating field and the frequency separation between the participating nuclear spin states [1]. A schematic depiction of the resonance phenomenon in a spin $I=1/2$ system is indicated in Figure 1.1

$$\omega_0 = \gamma B_0 \tag{1.1}$$

In accord with other forms of spectroscopy, the sensitivity of NMR transitions depends on the population difference between the nuclear spin states. From a

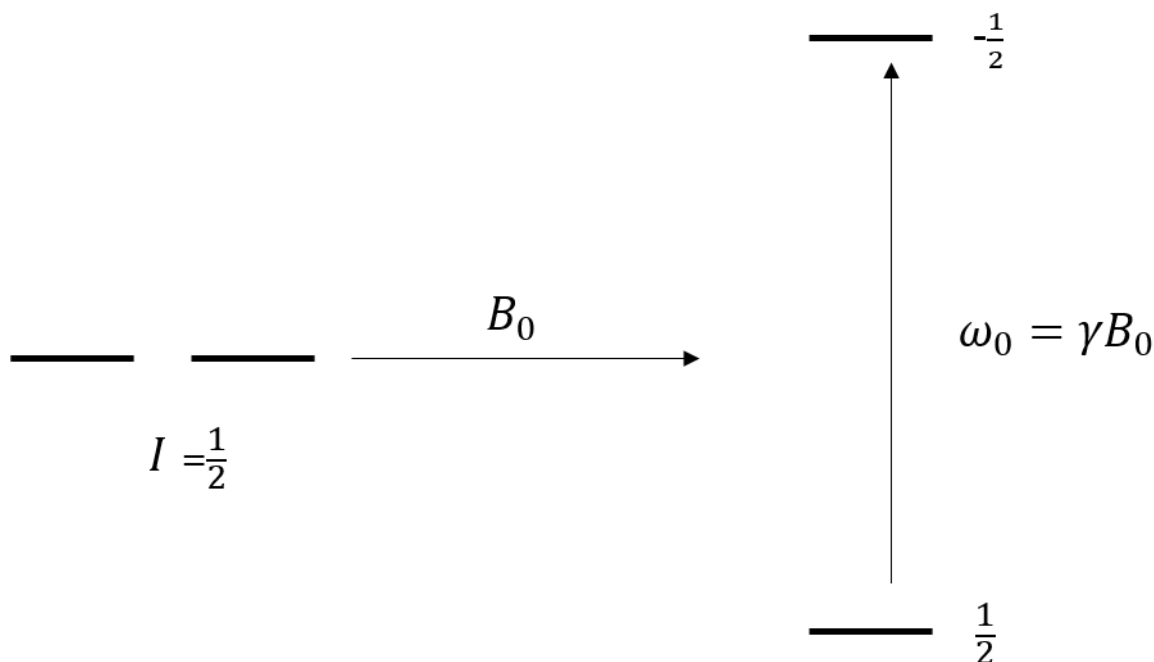


FIGURE 1.1: Schematic depiction of the resonance phenomenon in NMR spectroscopy (spin $I = \frac{1}{2}$)

classical perspective, this in turn depends on the transition probability amplitudes. In NMR spectroscopy, the transition probability amplitude depends on an intrinsic property of a particular nucleus and is commonly referred to as the 'nuclear gyromagnetic ratio'. The gyromagnetic ratio is inversely proportional to the mass of the nucleus and plays an important role in the sensitivity of a given NMR transition. In addition to the nuclear gyromagnetic ratio, the sensitivity in NMR also depends on the strength of the external magnetic field. Nevertheless, the cost factor involved in the design of high field magnets has been the main motivation behind the development of alternate strategies for improving the sensitivity in NMR spectroscopy. Besides these properties, the sensitivity also depends on the natural abundance of a particular isotope. Although, isotopic enrichment seems to be a viable alternative to compensate for the "natural abundance" factor, the dependence on the nuclear gyromagnetic ratio remains the major stumbling block. In particular, NMR studies involving less abundant nuclei such as, ^{13}C , ^{15}N nuclei remain severely hampered by their lower gyromagnetic ratios. To overcome this inherent limitation, alternate strategies in the form of cross-polarization (CP), dynamic nuclear polarization (DNP) and other sensitivity enhancement techniques

have emerged in magnetic resonance. The common strategy in such techniques involves the transfer of polarization from nuclei with higher gyromagnetic ratio to lesser sensitive nuclei. In the case of CP experiments, the abundant polarization from protons is transferred to the less-abundant nuclei (such as ^{13}C , ^{15}N) through double resonance experiments. In a similar vein, the polarization from electrons is transferred to nuclear spins in DNP experiments. In addition to improving the sensitivity, the above techniques have a profound effect on the spin-lattice relaxation time (lower the spin-lattice relaxation time) and have facilitated in the implementation of multi-dimensional experiments involving both less abundant and less sensitive nuclei.

In this thesis, we make an attempt to explain the mechanism of polarization transfer in such experiments. In chapter-2, the general methodology, transformations of spin Hamiltonians and conventions employed in the description of NMR experiments is discussed using the density operator formalism. The mechanism of polarization transfer in heteronuclear and homonuclear systems is discussed in chapter-3 and chapter-4 respectively. Employing effective Hamiltonians and the density operator formalism, analytic expressions depicting polarization transfer polarization transfer in isolated spin pair is discussed through suitable model systems and Hamiltonians that resemble to the ones employed in NMR (both solids and liquids). In chapter-5, the calculations presented in chapter-3 are extended to multiple-spin systems is discussed along with a brief note on the possible extensions of the present work.

Chapter 2

Understanding Transformation in NMR Through Density Operator Formalism

In quantum mechanics, the state of a system at a given instant of time, t is completely specified by a function $\Psi(r, t)$, where r is representative of the spatial degrees of the system. The function $\Psi(r, t)$ is commonly referred to as the wave function or state function and plays a central role in calculating the observable associated with the system. Based on Born's interpretation, the wave function represents the probability amplitude (or label) and the product $\Psi(r, t) * \Psi(r, t)$ the probability density. The probability of locating a particle in a given region of space, say volume element $d\tau$ is evaluated by multiplying the probability density with the volume element, $d\tau$. For operational convenience, the wave function is normalized through the following condition,

$$\int_{-\infty}^{\infty} \Psi^*(r, t)\Psi(r, t)d\tau = 1 \quad (2.1)$$

In the Schrodinger formulation of Quantum Mechanics, the time-evolution of the system is a given state $\psi(r, t)$ is calculated by evaluating a first order differential

equation given below

$$i\hbar \frac{d}{dt} \Psi(t) = H \Psi(t) \quad (2.2)$$

The formal solution to the above equation is represented below

$$\Psi(t) = e^{\frac{-i}{\hbar} H t} \Psi(0) \quad (2.3)$$

The constant of integration $\Psi(0)$ is the state of the system at time $t = 0$ and $e^{\frac{-i}{\hbar} H t}$ is called the **Evolution operator**

When the Hamiltonian is time dependent, (H is $H(t)$), in the Evolution operator has a complicated form as illustrated below

$$\Psi'(t) = e^{\frac{-i}{\hbar} \int_0^t H_1'(t') dt'} \Psi(0) \quad (2.4)$$

2.1 Interaction Frame Transformation

In NMR spectroscopy, the evolution of a system is governed by both the external and internal Hamiltonians. The external interactions mainly result from the interaction between the nuclear spin magnetic moment and the magnetic fields (inclusive of static and oscillating magnetic fields). These interactions are depicted through the Zeeman and radio frequency (RF) pulse Hamiltonians, respectively. The internal interactions are represented through the chemical shift, scalar and dipolar interactions. A detailed description of these interactions is discussed in standard literature and has consciously been omitted in this thesis to avoid repetition. Since important molecular constraints are contained in the internal spin interactions, a framework that presents the time-evolution of the system under the internal Hamiltonian is desired. From a theoretical viewpoint, this is accomplished through a set of transformations, wherein the contributions from the dominant interactions (say external Hamiltonians) are approximately removed from the description.

2.1.1 Wave Function Approach

Let us consider a system governed by the Hamiltonian

$$H = H_0 + H_1 \quad (2.5)$$

In the above equation H_0 represents the dominant Hamiltonian and H_1 the weak interaction. Substituting this Hamiltonian in time dependent Schrödinger equation (Equation(2.2))

$$i\hbar \frac{d}{dt} \Psi(t) = (H_0 + H_1) \Psi(t) \quad (2.6)$$

Equation(2.6) gives time dependent Schrödinger equation in the lab frame. To eliminate the role of the dominant terms/interactions, the description in the lab frame is abandoned in favour of a representation in the interaction frame. The state of the system in the interaction frame, $\Psi'(t)$, can be represented as

$$\Psi'(t) = e^{\frac{i}{\hbar} H_0 t} \Psi(t) \quad (2.7)$$

Differentiating the Equation(2.8) with respect to time and multiplying through out with $i\hbar$ gives the Schrödinger equation in the interaction frame

$$i\hbar \frac{d}{dt} \Psi'(t) = -H_0 e^{\frac{i}{\hbar} H_0 t} \Psi'(t) + e^{\frac{i}{\hbar} H_0 t} i\hbar \frac{d}{dt} \Psi(t) \quad (2.8)$$

Substituting Equation(2.7)

$$i\hbar \frac{d}{dt} \Psi'(t) = -H_0 e^{\frac{i}{\hbar} H_0 t} \Psi'(t) + e^{\frac{i}{\hbar} H_0 t} (H_0 + H_1) \Psi(t) \quad (2.9)$$

and the time evolution in the interaction frame is derived and described below

$$i\hbar \frac{d}{dt} \Psi'(t) = H'_1(t) \Psi'(t) \quad (2.10)$$

where $H'_1(t)$ denotes the modulated Hamiltonian, represented by

$$H'_1(t) = e^{\frac{i}{\hbar} H_0 t} H_1 e^{-\frac{i}{\hbar} H_0 t} \quad (2.11)$$

The Hamiltonian in the interaction frame, obtained by the unitary transformation UHU^\dagger is time dependent. Subsequently the time evolution of the system in the interaction frame is represented by

$$\Psi'(t) = e^{-\frac{i}{\hbar} \int_0^t H_1'(t) dt} \Psi'(0) \quad (2.12)$$

with $\Psi'(0) = \Psi(0)$, i.e., the initial state of the system.

When the Hamiltonian H_1 commutes with H_0 , the Hamiltonian is reduced to a much simpler form

$$H_1'(t) = H_1 \quad (2.13)$$

Then the state of the system at time, t , is

$$\Psi(t) = e^{-\frac{i}{\hbar} H_1 t} \Psi(0) \quad (2.14)$$

As depicted in Equation(2.12), the Hamiltonian in the interaction frame is time-dependent due to the frame transformation. To derive the solution, both numerical and analytic methods have been employed in the past. In the numerical methods, the total time duration is divided into shorter time intervals, wherein, the time-dependent Hamiltonian is approximated by a time independent Hamiltonian.

For example consider the evolution of a system from 0 to t , with initial state $\Psi(0)$. The total time from 0 to t is divided into N parts with duration t_i , ($i = 1, 2, \dots, N$), such that the evolution of the system during these intervals is described by a time-independent Hamiltonian, H_i . The evolution of the system at time t is obtained by taking the product over all such durations.

$$\psi(t) = e^{-\frac{i}{\hbar} H_N t_N} \psi(t - t_N) \quad (2.15)$$

$$\psi(t) = e^{-\frac{i}{\hbar} H_N t_N} e^{-\frac{i}{\hbar} H_{N-1} t_{N-1}} \dots e^{-\frac{i}{\hbar} H_1 t_1} \psi(0) \quad (2.16)$$

When the Hamiltonians at different times commute, the above equation reduces to a much simpler form.

$$\psi(t) = e^{\frac{-i}{\hbar} \sum_{i=1}^N H_i t_i} \psi(0) \quad (2.17)$$

As an alternate to numerical methods, in the analytic approach, the time-evolution of the system is described through time-averaged or effective Hamiltonians. A brief description of this method would be given in the following sections through appropriate examples.

$$\psi(t) = e^{\frac{-i}{\hbar} H_{eff} t} \psi(0) \quad (2.18)$$

2.1.2 Density Matrix Approach

When the state of system is not describable by a single wave function, then such a system is said to exist in a mixed state. In such cases, the state of a system is described by the density operator, $\rho(t)$. Analogous to the description in the wave function approach, the time-evolution of the system is described by the **Quantum Liouville (QL) theorem**.

$$i\hbar \frac{d}{dt} \rho(t) = [H, \rho(t)] \quad (2.19)$$

where $H = H_0 + H_1$.

$$i\hbar \frac{d}{dt} \rho(t) = [H_0 + H_1, \rho(t)] \quad (2.20)$$

The formal solution to the above equation is expressed by the unitary transformation $\rho(t) = U^\dagger \rho(0) U$. The unitary operator $U = e^{\frac{i}{\hbar} H t}$ is the evolution operator

$$\rho(t) = e^{\frac{-i}{\hbar} H t} \rho(0) e^{\frac{i}{\hbar} H t} \quad (2.21)$$

To describe the evolution of the system in terms of H_1 , let us define

$$\tilde{\rho}(t) = e^{\frac{i}{\hbar} H_0 t} \rho(t) e^{\frac{-i}{\hbar} H_0 t} \quad (2.22)$$

Substituting $\tilde{\rho}(t)$ in the L.H.S. of Equation(2.19), ie., taking derivative with respect to time and multiplying by $i\hbar$,

$$i\hbar \frac{d}{dt} \tilde{\rho}(t) = H_0 e^{\frac{i}{\hbar} H_0 t} \rho(t) e^{-\frac{i}{\hbar} H_0 t} + i\hbar e^{\frac{i}{\hbar} H_0 t} \frac{d}{dt} \rho(t) e^{-\frac{i}{\hbar} H_0 t} - e^{\frac{i}{\hbar} H_0 t} \rho(t) H_0 e^{-\frac{i}{\hbar} H_0 t} \quad (2.23)$$

Substitute Equation(2.20) the QL equation in the interaction frame reduces to a much simpler form

$$i\hbar \frac{d}{dt} \tilde{\rho}(t) = [H'_1(t), \tilde{\rho}(t)] \quad (2.24)$$

where

$$H'_1(t) = e^{\frac{i}{\hbar} H_0 t} H_1 e^{-\frac{i}{\hbar} H_0 t} \quad (2.25)$$

and the solution of differential equation in Equation(2.26), the density operator at time in the interaction frame is

$$\tilde{\rho}(t) = e^{-\frac{i}{\hbar} \int_0^t H'_1(t) dt} \tilde{\rho}(0) e^{\frac{i}{\hbar} \int_0^t H'_1(t) dt} \quad (2.26)$$

but the initial state of the system in both the frames are equal, $\tilde{\rho}(0) = \rho(0)$

2.2 Application of Interaction frame Transformation in NMR

We have two kinds of external magnetic fields used in NMR experiments, Static magnetic field, B_0 , along the Z axis which shifts degeneracy of the spin states and create a net magnetization long the Z direction

$$\vec{B}_0 = B_0 \hat{z} \quad (2.27)$$

and an Oscillating magnetic field, $B_1(t)$, along a direction perpendicular to the applied static field. It enables excitation from one state to the other. So we are interested in the effect of the RF pulse alone. The RF field below is along X axis

$$\vec{B}_1(t) = 2B_1 \cos(\omega t) \hat{x} \quad (2.28)$$

Zeeman energy, E , of interaction between the magnetic field and spin equals to dot product of the magnetic field, \vec{B} , with the magnetic dipole moment, $\vec{\mu}$, of the spin.

$$E = -\vec{\mu} \cdot \vec{B} \quad (2.29)$$

The magnetic dipole moment of the spin is $\gamma\hbar$ times the total spin angular momentum where γ is the Gyromagnetic ratio.

$$\mu = \gamma\hbar\hat{I} \quad (2.30)$$

Since static magnetic field is along Z axis only Z component of the the dipole moment contribute to the Zeeman interaction energy

$$E_z = -\vec{\mu} \cdot \vec{B}_0 \quad (2.31)$$

$$E_z = -\hbar\gamma B_0 I_z \quad (2.32)$$

$$E_z = -\hbar\omega_0 I_z = H_0 \quad (2.33)$$

where $\omega_0 = \gamma B_0$ is isotropic part of chemical shift. Likewise the interaction due to Oscillating magnetic field is

$$E_x = -\vec{\mu} \cdot \vec{B}_1(t) \quad (2.34)$$

$$E_x = -2\hbar\gamma B_1 \cos(\omega t) I_x \quad (2.35)$$

$$E_x = -2\hbar\omega_1 \cos \omega t I_x = H_1(t) \quad (2.36)$$

where $\omega_1 = \gamma B_1$ is the amplitude of RF interaction. Thus the total Zeeman Hamiltonian is given by the sum of static and oscillating magnetic field interactions.

$$H(t) = -\hbar\omega_0 I_z - 2\hbar\omega_1 \cos(\omega t) I_x \quad (2.37)$$

2.2.1 Effect of pulse on the system.

Consider the single pulse sequence depicted in FIGURE 2.1 during the time interval 0 to t_p (A strong intense RFV pulse of duration t_p is applied along the transverse plane). The static field applied to the system induces a net magnetisation along Z direction.

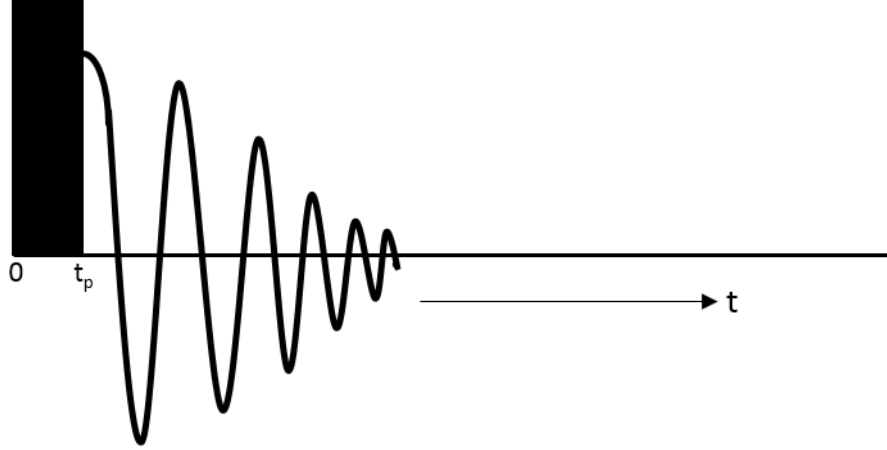


FIGURE 2.1: Schematic representation of a single pulse experiment with pulse duration t_p .

In addition to the static magnetic field, the system also experiences an oscillating magnetic field during the time interval 0 to t_p . The Hamiltonian of the system is represented by

$$H(t) = -\hbar\omega_0 I_z - 2\hbar\omega_1 \cos(\omega t) I_x \quad (2.38)$$

To describe the effect of the RF pulse the Hamiltonian defined in the lab frame is transformed into an interaction frame defined by the unitary transformation $U = e^{i\omega_0 t I_z}$.

$$H'_1(t) = -2\hbar\omega_1 \cos(\omega t) e^{-i\omega_0 t I_z} I_x e^{i\omega_0 t I_z} \quad (2.39)$$

$$H'_1(t) = -\hbar\omega_1 I_x [\cos(\omega_0 + \omega)t + \cos(\omega_0 - \omega)t] - \hbar\omega_1 I_y [\sin(\omega_0 + \omega)t + \sin(\omega_0 - \omega)t] \quad (2.40)$$

On resonance, we have $\omega = \omega_0$. Then,

$$H'_1(t) = -\hbar\omega_1 I_x - \hbar\omega_1 I_x \cos(2\omega_0 t) - \hbar\omega_1 I_y \sin(2\omega_0 t) \quad (2.41)$$

In the Zeeman interaction frame the RF Hamiltonian is explicitly time dependent and the solution for the Time dependent Schrödinger equation (Equation(2.10)) is not analytically solvable. Therefore, to calculate the state of the system in the interaction frame, we have to approximate the time dependent Hamiltonian to a time independent effective Hamiltonian (H_{eff}).

Invoking secular approximation, the high frequency oscillating terms in Equation(2.41)are neglected and the Hamiltonian is approximated to a time independent effective Hamiltonian.

$$H'_1(t) \simeq -\hbar\omega_1 I_x = H'_{1eff} \quad (2.42)$$

2.2.2 Wave Function Approach

The state of the system in the interaction frame is given by wave function,

$$\Psi'(t_p) = e^{i\omega_1 t I_x} \Psi(0) \quad (2.43)$$

where $\Psi(0)$ depicts the state at time zero, ie before applying the pulse. Accordingly, the expectation value of any operator $O_p(t)$ is evaluated using the standard expression

$$\langle O_p(t) \rangle = \frac{\langle \Psi(t) | O_p | \Psi(t) \rangle}{\langle \Psi(t) | \Psi(t) \rangle} \quad (2.44)$$

Employing this formula the expectation values of the spin angular momentum along X,Y and Z directions are evaluated.

$$\langle I_z \rangle = \frac{\langle \psi'(0) e^{-i\theta I_x} | I_z | e^{i\theta I_x} \psi'(0) \rangle}{\langle \psi'(0) | \psi'(0) \rangle} = \frac{\langle \Psi(0) | \cos(\omega_1 t) I_z - \sin(\omega_1 t) I_y | \Psi(0) \rangle}{\langle \Psi(0) | \Psi(0) \rangle} \quad (2.45)$$

$$\langle I_x \rangle = \frac{\langle \psi'(t_p) | I_x | \psi'(t_p) \rangle}{\langle \psi'(t_p) | \psi'(t_p) \rangle} = \frac{\langle \Psi(0) | I_x | \Psi(0) \rangle}{\langle \Psi(0) | \Psi(0) \rangle} \quad (2.46)$$

$$\langle I_y \rangle = \frac{\langle \psi'(0) e^{-i\theta I_x} | I_y | e^{i\theta I_x} \psi'(0) \rangle}{\langle \psi'(0) | \psi'(0) \rangle} = \frac{\langle \Psi(0) | I_y \cos(\omega_1 t) + I_x \sin(\omega_1 t) | \Psi(0) \rangle}{\langle \Psi(0) | \Psi(0) \rangle} \quad (2.47)$$

That is when pulse is applied along X axis, there is no change in the net magnetisation along X axis. and change in the magnetization happens in Z and Y

directions

As illustrated above, the expectation value depends on the initial state of the system. Below we illustrate this with few examples.

The wave function of the system is always a linear combination of the basis state $\{|\alpha\rangle, |\beta\rangle\}$, which is orthonormal.

Case 1: $\Psi(0) = |\alpha\rangle$

Suppose the system is initially in the pure state $\Psi(0) = |\alpha\rangle$. The components of the magnetization in the longitudinal and transverse plane are represented by,

$$\langle I_z \rangle = \langle \alpha | \cos(\omega_1 t) I_z - \sin(\omega_1 t) I_y | \alpha \rangle = \frac{\cos(\omega_1 t)}{2} \quad (2.48)$$

$$\langle I_x \rangle = \langle \alpha | I_x | \alpha \rangle = 0 \quad (2.49)$$

$$\langle I_y \rangle = \langle \alpha | \cos(\omega_1 t) I_y + \sin(\omega_1 t) I_z | \alpha \rangle = \frac{\sin(\omega_1 t)}{2} \quad (2.50)$$

Thus the magnetization of the system along Z axis is modulated by cosine function, while along Y axis it is modulated by the sin function.

At $t = 0$, before the pulse is applied, the total magnetization is along the Z axis with no magnetization in the X or Y axes.

$$(2.51)$$

$$\langle I_z \rangle = \frac{1}{2} \quad (2.52)$$

$$\langle I_x \rangle = 0 \quad (2.53)$$

$$\langle I_y \rangle = 0 \quad (2.54)$$

If we have a 90° X pulse $\omega_1 t_p = \frac{\pi}{2}$ after the pulse total magnetization flipped to Y direction from Z by a positive rotation along the direction of the pulse

$$(2.55)$$

$$\langle I_z \rangle = 0 \quad (2.56)$$

$$\langle I_x \rangle = 0 \quad (2.57)$$

$$\langle I_y \rangle = \frac{1}{2} \quad (2.58)$$

The net magnetisation along X direction is always zero through out the application of pulse. After a 90° pulse along X axis there will be no net magnetisation along Z direction.

Case 2: $\Psi(0) = |\beta\rangle$

Considering the system initially in the pure state $\Psi(0) = |\beta\rangle$. In a Similar fashion magnetization has the following components of angular momentum

$$\langle I_z \rangle = \langle \beta | \cos(\omega_1 t) I_z - \sin(\omega_1 t) I_y | \beta \rangle = \frac{-\cos(\omega_1 t)}{2} \quad (2.59)$$

$$\langle I_x \rangle = \langle \beta | I_x | \beta \rangle = 0 \quad (2.60)$$

$$\langle I_y \rangle = \langle \beta | \cos(\omega_1 t) I_y + \sin(\omega_1 t) I_z | \beta \rangle = \frac{-\sin(\omega_1 t)}{2} \quad (2.61)$$

Before the pulse, $t = 0$, total magnetization is along -Z axis with no magnetization in X or Y directions.

$$(2.62)$$

$$\langle I_z \rangle = \frac{-1}{2} \quad (2.63)$$

$$\langle I_x \rangle = 0 \quad (2.64)$$

$$\langle I_y \rangle = 0 \quad (2.65)$$

Gradually it rotates clockwise along X axis, flipping total magnetization along -Y axis after a 90° X pulse.

$$\langle I_z \rangle = 0 \quad (2.66)$$

$$\langle I_x \rangle = 0 \quad (2.67)$$

$$\langle I_y \rangle = \frac{-1}{2} \quad (2.68)$$

Case 3: $\Psi(0) = C_\alpha|\alpha\rangle + C_\beta|\beta\rangle$

Consider the system initially in a state which is linear combination of the basis states $\Psi(0) = C_\alpha|\alpha\rangle + C_\beta|\beta\rangle$. Accordingly, the expectation values are evaluated

$$\langle I_z \rangle = \frac{\cos(\omega_1 t)(C_\alpha^* C_\alpha - C_\beta^* C_\beta) - i \sin(\omega_1 t)(C_\beta^* C_\alpha - C_\alpha^* C_\beta)}{2(C_\alpha^* C_\alpha + C_\beta^* C_\beta)} \quad (2.69)$$

$$\langle I_x \rangle = \frac{C_\beta^* C_\alpha + C_\alpha^* C_\beta}{2(C_\alpha^* C_\alpha + C_\beta^* C_\beta)} \quad (2.70)$$

$$\langle I_y \rangle = \frac{\sin(\omega_1 t)(C_\alpha^* C_\alpha - C_\beta^* C_\beta) + i \cos(\omega_1 t)(C_\beta^* C_\alpha - C_\alpha^* C_\beta)}{2(C_\alpha^* C_\alpha + C_\beta^* C_\beta)} \quad (2.71)$$

Before the pulse,

$$\langle I_z \rangle = \frac{1}{2} \frac{C_\alpha^* C_\alpha - C_\beta^* C_\beta}{C_\alpha^* C_\alpha + C_\beta^* C_\beta} \quad (2.72)$$

$$\langle I_x \rangle = \frac{1}{2} \frac{C_\beta^* C_\alpha + C_\alpha^* C_\beta}{C_\alpha^* C_\alpha + C_\beta^* C_\beta} \quad (2.73)$$

$$\langle I_y \rangle = \frac{i}{2} \frac{C_\beta^* C_\alpha - C_\alpha^* C_\beta}{C_\alpha^* C_\alpha + C_\beta^* C_\beta} \quad (2.74)$$

and after the 90° X pulse,

$$\langle I_z \rangle = \frac{i}{2} \frac{C_\beta^* C_\alpha - C_\alpha^* C_\beta}{C_\alpha^* C_\alpha + C_\beta^* C_\beta} \quad (2.75)$$

$$\langle I_x \rangle = \frac{1}{2} \frac{C_\beta^* C_\alpha + C_\alpha^* C_\beta}{C_\alpha^* C_\alpha + C_\beta^* C_\beta} \quad (2.76)$$

$$\langle I_y \rangle = \frac{1}{2} \frac{C_\alpha^* C_\alpha - C_\beta^* C_\beta}{C_\alpha^* C_\alpha + C_\beta^* C_\beta} \quad (2.77)$$

The net magnetisation along X direction is always constant through out the application of pulse. After a 90° pulse along X axis, implies after a pulse along X axis for a time $t_p = \frac{\pi}{2\omega_1}$ the net magnetisation along Z flipped to Y direction and along Y flipped to Z direction by a positive rotation along the direction of the pulse.

2.2.3 Density Matrix Approach

When state of the system is described by density operator the time evolution of a density operator follows the QL theorem and the effective Hamiltonian in the Zeeman interaction frame is described by

$$H'_{1eff} = -\hbar\omega_1 I_x \quad (2.78)$$

The state of the system at $t = 0$ is represented by

$$\tilde{\rho}(0) = I_z \quad (2.79)$$

the evolution under the effective Hamiltonian is described as

$$\tilde{\rho}(t) = e^{i\omega_1 t I_x} I_z e^{-i\omega_1 t I_x} = \cos(\omega_1 t) I_z + \sin(\omega_1 t) I_y \quad (2.80)$$

The expectation value of any operator, O_p is obtained by the standard formula

$$\langle O_p(t) \rangle = \text{Trace}(O_p(t) \cdot \tilde{\rho}(t)) \quad (2.81)$$

Accordingly the expectation value of angular momentum operators during pulse are given by the following formula

$$\langle I(t) \rangle = \text{Trace} \begin{bmatrix} \frac{1}{4} \cos(\omega_1 t) & \frac{-i}{4} \sin(\omega_1 t) \\ \frac{i}{4} \sin(\omega_1 t) & \frac{-1}{4}(\omega_1 t) \end{bmatrix} = 0 \quad (2.82)$$

$$\langle I_x(t) \rangle = \text{Trace} \begin{bmatrix} \frac{i}{4} \sin(\omega_1 t) & \frac{-1}{4} \cos(\omega_1 t) \\ \frac{1}{4} \cos(\omega_1 t) & \frac{-i}{4} \sin(\omega_1 t) \end{bmatrix} = 0 \quad (2.83)$$

$$\langle I_y(t) \rangle = \text{Trace} \begin{bmatrix} \frac{1}{4} \sin(\omega_1 t) & \frac{i}{4} \cos(\omega_1 t) \\ \frac{i}{4} \cos(\omega_1 t) & \frac{1}{4} \sin(\omega_1 t) \end{bmatrix} = \frac{1}{2} \sin(\omega_1 t) \quad (2.84)$$

$$\langle I_z(t) \rangle = \text{Trace} \begin{bmatrix} \frac{1}{4} \cos(\omega_1 t) & \frac{-i}{4} \sin(\omega_1 t) \\ \frac{-i}{4} \sin(\omega_1 t) & \frac{1}{4} \cos(\omega_1 t) \end{bmatrix} = \frac{1}{2} \cos(\omega_1 t) \quad (2.85)$$

Thus at $t = 0$ the expectation values of only Z component of angular momentum was non-zero

$$\langle I_z(0) \rangle = \frac{1}{2} \quad (2.86)$$

$$\langle I_x(0) \rangle = 0 \quad (2.87)$$

$$\langle I_y(0) \rangle = 0 \quad (2.88)$$

after a $\frac{\Pi}{2}$ X pulse the Z component became zero and the spin got flipped to Y direction

$$\langle I_z(t_p) \rangle = 0 \quad (2.89)$$

$$\langle I_x(t_p) \rangle = 0 \quad (2.90)$$

$$\langle I_y(t_p) \rangle = \frac{1}{2} \quad (2.91)$$

After the pulse duration, t_p , The system evolve under the static magnetic field and Hamiltonian describing the evolution is H_0 .

$$\rho(t_p + t) = e^{\frac{i}{\hbar} H_z t} \rho(t_p) e^{-\frac{i}{\hbar} H_z t} \quad (2.92)$$

Transformation to the interaction frame depicts the state of the system after the pulse as

$$\begin{aligned} \tilde{\rho}(t_p + t) &= e^{\frac{i}{\hbar} H_z (t_p + t)} \rho(t_p + t) e^{-\frac{i}{\hbar} H_z (t_p + t)} \\ &= e^{\frac{i}{\hbar} H_z (t_p + t)} e^{-\frac{i}{\hbar} H_z t} \rho(t_p) e^{\frac{i}{\hbar} H_z t} e^{-\frac{i}{\hbar} H_z (t_p + t)} \\ &= e^{\frac{i}{\hbar} H_z t_p} \rho(t_p) e^{-\frac{i}{\hbar} H_z t_p} \end{aligned}$$

$$\tilde{\rho}(t_p + t) = \tilde{\rho}(t_p) \quad (2.93)$$

State of the system does not change in the interaction frame because the in the interaction frame H_0 has no effect. But the actual signal gives an oscillating signal. This contradiction raised because even though we are working in the interaction frame the detection operators are all in the lab frame .In order to evaluate the signal in the interaction frame we need to transform the detection operators also to the interaction frame. Any operator $O_p(t)$ is transformed into the interaction frame by

$$\tilde{O}_p = e^{\frac{i}{\hbar}H_{eff}t}O_p e^{-\frac{i}{\hbar}H_{eff}t} \quad (2.94)$$

Thus in this frame the components of angular momentum are

$$\tilde{I}_z(t) = e^{-i\omega_0 t I_z} I_z e^{i\omega_0 t I_z} = I_z \quad (2.95)$$

$$\tilde{I}_y(t) = e^{-i\omega_0 t I_z} I_y e^{i\omega_0 t I_z} = \cos\theta_0 I_y - \sin\theta_0 I_x \quad (2.96)$$

$$\tilde{I}_x(t) = e^{-i\omega_0 t I_z} I_x e^{i\omega_0 t I_z} = \cos\theta_0 I_x + \sin\theta_0 I_y \quad (2.97)$$

Accordingly the expectation value of angular momentum are evaluated by Equation(2.81)

$$\langle \tilde{I}_z(t) \rangle = \frac{1}{2} \cos(\omega_1 t) \quad (2.98)$$

$$\langle \tilde{I}_y(t) \rangle = \frac{1}{2} \cos\theta_0 \sin(\omega_1 t) \quad (2.99)$$

$$\langle \tilde{I}_x(t) \rangle = \frac{1}{2} \sin\theta_0 \sin(\omega_1 t) \quad (2.100)$$

Subsequently at $t = 0$

$$\langle \tilde{I}_z(0) \rangle = \frac{1}{2} \quad (2.101)$$

$$\langle \tilde{I}_x(0) \rangle = 0 \quad (2.102)$$

$$\langle \tilde{I}_y(0) \rangle = 0 \quad (2.103)$$

and after the $\frac{\pi}{2}$ pulse

$$\langle \tilde{I}_z(t_p + t) \rangle = 0 \quad (2.104)$$

$$\langle \tilde{I}_x(t_p + t) \rangle = \frac{1}{2} \sin(\omega_0 t) \quad (2.105)$$

$$\langle \tilde{I}_y(t_p + t) \rangle = \frac{1}{2} \cos(\omega_0 t) \quad (2.106)$$

After the pulse the magnetization along Z flipped to X-Y plane (transverse plane), and it oscillates in both X and Y direction. But the actual FID is damping. Considering exponential damping

$$\tilde{\rho}(t) = e^{-\frac{i}{\hbar} H'_{eff} t} \tilde{\rho}(0) e^{\frac{i}{\hbar} H'_{eff} t} e^{-\frac{t}{T_2}} \quad (2.107)$$

Where T_2 is the damping constant. Corresponding angular momentum values also will be having the damping term.

$$\langle \tilde{I}_z \rangle = \frac{1}{2} \cos\theta_1 e^{-\frac{t}{T_2}} \langle \tilde{I}_y \rangle = \frac{1}{2} \cos\theta_0 \sin\theta_1 e^{-\frac{t}{T_2}} \langle \tilde{I}_x \rangle = \frac{1}{2} \sin\theta_0 \sin\theta_1 e^{-\frac{t}{T_2}} \quad (2.108)$$

When the RF pulse applied have a phase $\phi \neq 0$ The RF interaction Hamiltonian is depicted as

$$H_{RF} = -2\hbar\omega_1 \cos(\omega t - \phi) I_x \quad (2.109)$$

and in the interaction frame it is represented by the following formula by employing secular approximation

$$H'_1 \simeq H'_{1eff} = -\hbar\omega_1 [I_x \cos\phi + I_y \sin\phi] \quad (2.110)$$

The expectation value of components of angular momentum for different ϕ value are given in table below

	$\phi = 0$	$\phi = \frac{\pi}{2}$	$\phi = \pi$	$\phi = \frac{3\pi}{2}$
$\langle \tilde{I}_z \rangle$	0	0	0	0
$\langle \tilde{I}_x \rangle$	$\frac{1}{2} \sin(\omega_0 t)$	$-\frac{1}{2} \cos(\omega_0 t)$	$-\frac{1}{2} \sin(\omega_0 t)$	$\frac{1}{2} \cos(\omega_0 t)$
$\langle \tilde{I}_y \rangle$	$\frac{1}{2} \cos(\omega_0 t)$	$\frac{1}{2} \sin(\omega_0 t)$	$-\frac{1}{2} \cos(\omega_0 t)$	$-\frac{1}{2} \sin(\omega_0 t)$
$\langle \tilde{I}_+ \rangle$	$\frac{i}{2} e^{-i\omega_0 t}$	$-\frac{1}{2} e^{-i\omega_0 t}$	$\frac{i}{2} e^{-i\omega_0 t}$	$\frac{1}{2} e^{-i\omega_0 t}$
$\langle \tilde{I}_- \rangle$	$\frac{i}{2} e^{i\omega_0 t}$	$-\frac{1}{2} e^{i\omega_0 t}$	$\frac{i}{2} e^{i\omega_0 t}$	$\frac{1}{2} e^{i\omega_0 t}$

2.2.4 Effect of Pulse on the System in Rotating Frame

In the rotating frame, we have the state of the system at t_p ,

$$\rho(\tilde{t}_p) = e^{(-i\omega_{ref} t_p I_z)} \rho(t_p) e^{(i\omega_{ref} t_p I_z)} \quad (2.111)$$

$$i\hbar \frac{d\tilde{\rho}(t)}{dt} = [-\hbar(\omega_0 - \omega_{ref}) I_z, \tilde{\rho}(t)] + [H'_1, \tilde{\rho}(t)] \quad (2.112)$$

$(\omega_0 - \omega_{ref}) = \Delta\omega$. ie, the chemical shift.

$$[i\hbar \frac{d\tilde{\rho}}{dt}(t) = [-\hbar\Delta\omega I_z, \tilde{\rho}(t)] + [H'_1, \tilde{\rho}(t)] \quad (2.113)$$

Where,

$$H'_1 = -2\hbar\omega_1 \cos(\omega t - \phi) e^{-i\omega_{ref} t I_z} I_x e^{i\omega_{ref} t I_z} = -2\hbar\omega_1 \cos(\omega t - \phi) [\cos\theta_{ref} I_x + \sin\theta_{ref} I_y] \quad (2.114)$$

On resonance, $\omega = \omega_{ref} \implies \theta = \theta_{ref}$ by implementing secular approximation, we omit the high frequency oscillating terms, Total hamiltonian in the new frame is,

$$\tilde{H} = -\hbar\Delta\omega I_z - \hbar\omega_1 [I_x \cos\phi + I_y \sin\phi]$$

During the pulse since $\omega_1 \gg \Delta\omega$, the Hamiltonian can be approximated as if only pulse is acting and there is no effect of B_0 .ie,

$$\tilde{H} \sim -\hbar\omega_1[I_x\cos\phi + I_y\sin\phi]$$

After pulse , the system evolve under ,

$$\tilde{H} = -\hbar\Delta\omega I_z$$

ie,in rotating lab frame the system evolve under $-\hbar\omega_1[\cos\phi I_x + \sin\phi I_y]$ during the pulse and $-\hbar\delta\omega I_z$

An operator \hat{A} in rotating frame becomes,

$$\tilde{A} = e^{(-i\omega_{ref}tI_z)} A e^{(i\omega_{ref}tI_z)}$$

We know $\omega_{ref}t = \theta_{ref}$

$$\begin{aligned}\tilde{I}_z &= I_z \\ \tilde{I}_x &= \cos\theta_{ref}I_x + \sin\theta_{ref}I_y \\ \tilde{I}_y &= \cos\theta_{ref}I_y - \sin\theta_{ref}I_x\end{aligned}$$

State of the system just after pulse, ie, at time t_p ,

$$\begin{aligned}\tilde{\rho}(t_p) &= e^{\frac{-i}{\hbar}\tilde{H}t} \tilde{\rho}(0) e^{\frac{i}{\hbar}\tilde{H}t} \\ \tilde{\rho}(0) &= \rho(0) \\ \tilde{H} &= -\hbar\omega_1[I_x\cos\phi + I_y\sin\phi]\end{aligned}$$

State of system at time $t_p + t$,

$$\begin{aligned}\tilde{\rho}(t_p + t) &= e^{\frac{-i}{\hbar}\tilde{H}t} \tilde{\rho}(t_p) e^{\frac{i}{\hbar}\tilde{H}t} \\ \tilde{H} &= -\hbar\Delta\omega I_z\end{aligned}$$

Find the magnetization along different directions for different phase of pulse (ϕ). We use the identities,

$$Tr[I_i, I_j] = \begin{cases} \frac{1}{2} & i = j \\ 0 & i \neq j \end{cases}$$

Where $i, j \in \{x, y, z\}$ **Case 1:** $\phi = 0$

$$\begin{aligned} \tilde{\rho}(t_p) &= e^{i\omega_1 I_x t} I_z e^{-i\omega_1 I_x t} \\ &= \cos\theta_1 I_z + \sin\theta_1 I_y \end{aligned}$$

$$\text{Where } \omega_1 t_p = \theta_1$$

If we adjust ω_1 such that,

$$\theta_1 = \frac{\pi}{2}$$

$$\tilde{\rho}(t_p) = I_y$$

Now after pulse, system evolve under $\tilde{H} = -\hbar\Delta\omega I_z$

$$\begin{aligned} \tilde{\rho}(t_p + t) &= e^{\frac{-i}{\hbar}\tilde{H}t} \tilde{\rho}(t_p) e^{\frac{i}{\hbar}\tilde{H}t} \\ &= e^{i\Delta\omega t I_z} I_y e^{-i\Delta\omega t I_z} \\ &= \cos\Delta\theta I_y + \sin\Delta\theta I_x \end{aligned}$$

$$\text{Where, } \Delta\theta = \Delta\omega t$$

Using the identities, we have

$$\begin{aligned} \langle \tilde{I}_z \rangle = 0 \quad \langle \tilde{I}_y \rangle &= \langle \cos\theta_{ref} I_y - \sin\theta_{ref} I_x \rangle \\ &= \frac{1}{2} [\cos\Delta\theta \cos(\theta_{ref}) - \sin\Delta\theta \sin\theta_{ref}] \\ &= \frac{1}{2} \cos(\omega_0 t) \\ \langle \tilde{I}_x \rangle &= \langle \cos\theta_{ref} I_x + \sin\theta_{ref} I_y \rangle \\ &= \frac{1}{2} [\sin\Delta\theta \cos(\theta_{ref}) + \cos\Delta\theta \sin\theta_{ref}] \\ &= \frac{1}{2} \sin(\omega_0 t) \end{aligned}$$

Case 2: $\phi = \frac{\pi}{2}$

$$\begin{aligned}\tilde{H} &= -\hbar\omega_1 I_y \\ \tilde{\rho}(t_p) &= e^{i\omega_1 t I_y} I_z e^{-i\omega_1 t I_y} \\ &= \cos\theta_1 I_z - \sin\theta_1 I_x\end{aligned}$$

When $\theta_1 = \omega_1 t_p = \frac{\pi}{2}$,

$$\begin{aligned}\tilde{\rho}(t_p) &= -I_x \\ \tilde{\rho}(t_p + t) &= e^{i\Delta\omega t I_z} (-I_x) e^{-i\Delta\omega t I_z} \\ &= \sin\Delta\theta I_y - \cos\Delta\theta I_x \\ \langle \tilde{I}_z \rangle &= 0 \\ \langle \tilde{I}_y \rangle &= \langle \cos\theta_{ref} I_y - \sin\theta_{ref} I_x \rangle \\ &= \frac{1}{2} [\sin\Delta\theta \cos(\theta_{ref}) + \cos\Delta\theta \sin\theta_{ref}] \\ &= \frac{1}{2} \sin(\omega_0 t) \\ \langle \tilde{I}_x \rangle &= \langle \cos\theta_{ref} I_x + \sin\theta_{ref} I_y \rangle \\ &= \frac{-1}{2} [\cos\Delta\theta \cos(\theta_{ref}) - \sin\Delta\theta \sin(\theta_{ref})] \\ &= \frac{-1}{2} \sin(\omega_0 t)\end{aligned}$$

Case 3: $\phi = \pi$

$$\begin{aligned}\tilde{\rho}(t_p) &= e^{-i\omega_1 t_p I_x} I_z e^{i\omega_1 t_p I_x} \\ &= \cos\theta_1 I_z - \sin\theta_1 I_y\end{aligned}$$

when $\theta = \omega_1 t_p = \frac{\pi}{2}$,

$$\begin{aligned}
 \tilde{\rho}(t_p) &= -I_y \\
 \tilde{\rho}(t_p + t) &= e^{i\Delta\omega t I_z} (-I_y) e^{-i\Delta\omega t I_z} \\
 &= -[\cos \Delta\theta I_y + \sin \Delta\theta I_x] \\
 \langle \tilde{I}_z \rangle &= 0 \\
 \langle \tilde{I}_y \rangle &= \langle \cos\theta_{ref} I_y - \sin\theta_{ref} I_x \rangle \\
 &= \frac{-1}{2} \cos(\omega_0 t) \\
 \langle \tilde{I}_x \rangle &= \langle \cos\theta_{ref} I_x + \sin\theta_{ref} I_y \rangle \\
 &= \frac{-1}{2} \sin(\omega_0 t)
 \end{aligned}$$

Case 4: $\phi = 3\frac{\pi}{2}$

$$\begin{aligned}
 \tilde{\rho}(t_p) &= e^{-i\omega_1 t_p I_y} I_z e^{i\omega_1 t_p I_y} \\
 &= \cos\theta_1 I_z + \sin\theta_1 I_x
 \end{aligned}$$

When $\theta_1 = \omega_1 t_p = \frac{\pi}{2} \implies \tilde{\rho}(t_p) = I_x$

$$\begin{aligned}
 \tilde{\rho}(t_p + t) &= e^{i\Delta\omega t I_z} (I_x) e^{-i\Delta\omega t I_z} \\
 &= [\cos\Delta\theta I_x - \sin\Delta\theta I_y] \\
 \langle \tilde{I}_z \rangle &= 0 \\
 \langle \tilde{I}_y \rangle &= \langle \cos\theta_{ref} I_y - \sin\theta_{ref} I_x \rangle \\
 &= \frac{-1}{2} \sin(\omega_0 t) \\
 \langle \tilde{I}_x \rangle &= \langle \cos\theta_{ref} I_x + \sin\theta_{ref} I_y \rangle \\
 &= \frac{1}{2} \cos(\omega_0 t)
 \end{aligned}$$

The results in both the frames are the same. And can be summarised as, Magnetization along different direction after pulse,

	$\phi = 0$	$\phi = \frac{\pi}{2}$	$\phi = \pi$	$\phi = \frac{3\pi}{2}$
$\langle \tilde{I}_z \rangle$	0	0	0	0
$\langle \tilde{I}_x \rangle$	$\frac{1}{2} \sin(\omega_0 t)$	$-\frac{1}{2} \cos(\omega_0 t)$	$-\frac{1}{2} \sin(\omega_0 t)$	$\frac{1}{2} \cos(\omega_0 t)$
$\langle \tilde{I}_y \rangle$	$\frac{1}{2} \cos(\omega_0 t)$	$\frac{1}{2} \sin(\omega_0 t)$	$-\frac{1}{2} \cos(\omega_0 t)$	$-\frac{1}{2} \sin(\omega_0 t)$
$\langle \tilde{I}_+ \rangle$	$\frac{i}{2} e^{-i\omega_0 t}$	$-\frac{i}{2} e^{\frac{i\pi}{2}} e^{-i\omega_0 t}$	$\frac{i}{2} e^{i\pi} e^{-i\omega_0 t}$	$\frac{i}{2} e^{\frac{i3\pi}{2}} e^{-i\omega_0 t}$
$\langle \tilde{I}_- \rangle$	$-\frac{i}{2} e^{i\omega_0 t}$	$-\frac{i}{2} e^{\frac{i\pi}{2}} e^{i\omega_0 t}$	$-\frac{i}{2} e^{i\pi} e^{i\omega_0 t}$	$-\frac{i}{2} e^{\frac{i3\pi}{2}} e^{i\omega_0 t}$

The results got in the interaction frame and rotating lab frame are exactly same. Also, in each case, the $\langle I_+ \rangle$ and $\langle I_- \rangle$ are complex conjugate of each other. From the table, the results can be generalized as follows,

$$\begin{aligned}
 \langle \tilde{I}_z \rangle &= 0 \\
 \langle \tilde{I}_x \rangle &= \frac{1}{2} \sin(\omega_0 t - \phi) \\
 \langle \tilde{I}_y \rangle &= \frac{1}{2} \cos(\omega_0 t - \phi) \\
 \langle \tilde{I}_+ \rangle &= \frac{i}{2} e^{-i(\omega_0 t - \phi)} \\
 \langle \tilde{I}_- \rangle &= \frac{-i}{2} e^{i(\omega_0 t - \phi)}
 \end{aligned}$$

In order to get rid of the phase factor $e^{i\phi}$ the detector phase has to be adjusted to $e^{-i\phi}$

Chapter 3

Polarization Transfer in Zero Quantum (ZQ) and Double Quantum (DQ) Experiments

3.1 Effective Hamiltonian For Two Spin Heteronuclear System

To describe the mechanism of polarization transfer in heteronuclear spin systems a model system comprising of two spins I and S was employed in the present study. The standard cross polarization(CP) experiment was employed as a case study.

The Hamiltonian for an isolated heteronuclear spin pair is represented by,

$$H(t) = H_{CS} + H_{RF}(t) + H_D \quad (3.1)$$

In the above equation H_z denotes the chemical shift (Zeeman) interaction

$$H_{CS} = -\omega_I I_z - \omega_S S_z \quad (3.2)$$

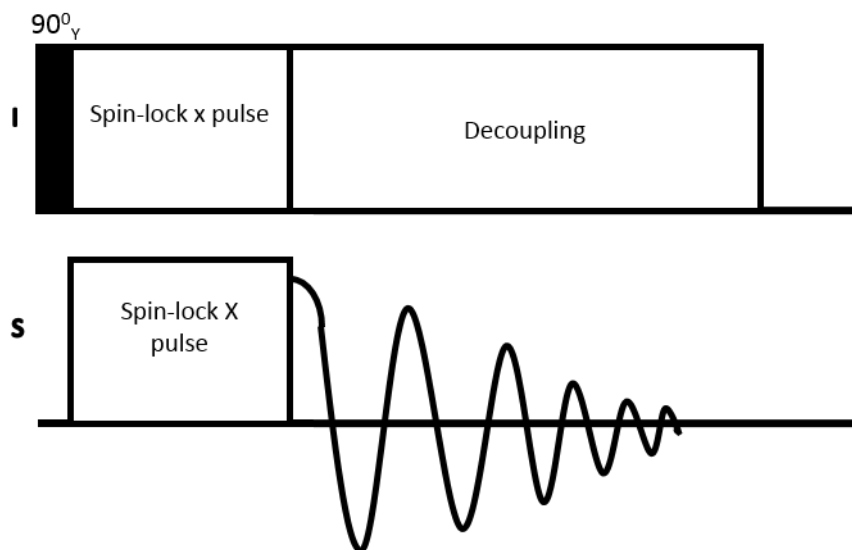


FIGURE 3.1: Schematic representation of pulse sequence for heteronuclear polarization transfer experiment (Cross Polarization experiments). The system consists of dipolar coupled heteronuclear spins I and S. Polarization is transferred from I spin to S spin

and H_{RF} the interaction due to RF field.

$$H_{RF}(t) = -2\omega_{1I} \cos(\omega_{rf,I}t)I_y - 2\omega_{1S} \cos(\omega_{rf,S}t)S_y \quad (3.3)$$

The dipolar interaction between the spins is represented by

$$H_D = 2\omega_d I_z S_z \quad (3.4)$$

In equation (3.2) ω_i ($i = I, S$) are the isotropic component of the chemical shielding interaction. (The anisotropic component of the chemical shielding interaction (CSA) is neglected). ω_{1I} and ω_{1S} in equation (3.3) are the amplitudes of the RF field in the I channel and the S channel respectively. The frequencies of the oscillating RF fields in I and S channels are respectively $\omega_{rf,I}$ and $\omega_{rf,S}$. ω_d in equation(3.4) is the dipolar coupling constant.

To know polarization transfer we want to know the effect of the dipolar interaction in the system, which is a minor interaction. An on resonance Zeeman interaction frame is introduced. The Hamiltonian is transformed by the unitary

transformation $\tilde{H} = U^\dagger H U$ where $U = e^{-i(-\omega_I I_z - \omega_S S_z)t}$

$$\tilde{H} = -\omega_I I_x - \omega_S S_x + 2\omega_d I_z S_z \quad (3.5)$$

In the Zeeman frame RF interaction which is the dominant interaction is along X axis. Introducing a tilted coordinate system the RF part of the Hamiltonian is quantized along the Z-direction to further simplify the calculation. This transformation $\tilde{H}_T = U_T^\dagger \tilde{H} U_T$ is performed using the unitary operator $U_T = e^{i\frac{\pi}{2} I_y} e^{i\frac{\pi}{2} S_y}$

$$\tilde{H}_T = \omega_I I_z + \omega_S S_z + 2\omega_d I_x S_x \quad (3.6)$$

In the tilted frame the heteronuclear dipolar interaction comprises of double quantum(DQ) and zero quantum (ZQ) operators.

$$\tilde{H}_T = \omega_I I_z + \omega_S S_z + \frac{\omega_d}{2}(I_+ S_+ + I_- S_-) + \frac{\omega_d}{2}(I_+ S_- + I_- S_+) \quad (3.7)$$

However the effective dipolar coupling constants for DQ and ZQ are equal and it is half of the coupling constant between the two spins.

$$C_d = \frac{\omega_d}{2} \quad (3.8)$$

Next to isolate different recoupling conditions the system is transformed to the RF interaction frame using the unitary operator $U = e^{-i(\omega_I I_z + \omega_S S_z)t}$ Hamiltonian in the interaction frame is given by

$$\tilde{\tilde{H}}_T = C_d \{ I_+ S_+ e^{-i(\omega_I + \omega_S)t} + I_- S_- e^{i(\omega_I + \omega_S)t} + I_+ S_- e^{-i(\omega_I - \omega_S)t} + I_- S_+ e^{i(\omega_I - \omega_S)t} \} \quad (3.9)$$

Thus recoupling occurs in DQ and ZQ terms. ZQ transfer occurs when the difference in RF field applied on both channels is Zero.

$$\Delta_{rf} = \omega_I - \omega_S = 0 \quad (3.10)$$

$$H_{eff} = C_d(I_+ S_- + I_- S_+) \quad (3.11)$$

Likewise DQ transfer happens when the RF in the two channels have π phase difference.

$$\sum_{RF} = \omega_I + \omega_S = 0 \quad (3.12)$$

$$H_{eff} = C_d(I_+S_+ + I_-S_-) \quad (3.13)$$

The ZQ and DQ recoupling conditions are called the Hartmann-Hahn Matching conditions. These conditions are used in cross polarization experiments.

3.2 Effective Hamiltonian For Two Spin Homonuclear System

An analytical model of the polarization transfer in broadband dipolar experiments can be used to measure homonuclear distances such as ^{13}C - ^{13}C in a sample. The Polarization from an abundant nuclei like ^1H is transferred to the I spin by heteronuclear polarization transfer experiment say in this case a CP experiment (FIGURE 4.1). The homonuclear polarization transfer in HORROR experiment occurs when $\omega_{rf} = \frac{\omega_r}{2}$ in the I channel between the two 90° Y pulse. This is the part of the pulse that we are considering.

For this we consider dipolar coupled N spin homonuclear system $\{S_i\}$ ($i = 1, 2, 3, \dots, N$) with a Hamiltonian, $H(t)$, that is time dependent due to sample spinning.

$$H(t) = H_{CS} + H_{CSA}(t) + H_D(t) + H_{RF} \quad (3.14)$$

The different parts of the Hamiltonian are the resonance offset,

$$H_{CS} = \sum_{i=1}^N \Omega_i I_{iz} \quad (3.15)$$

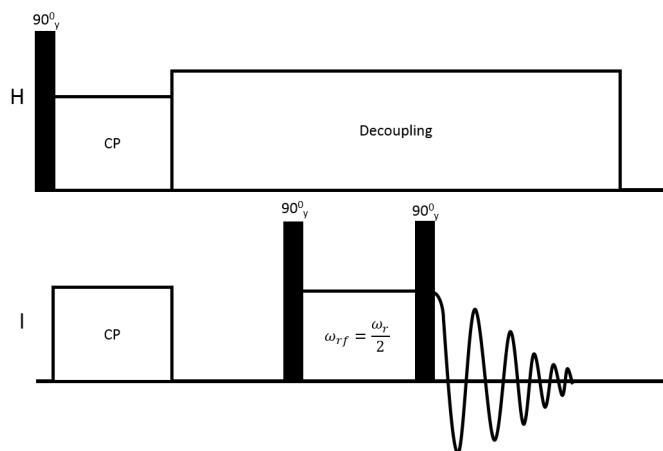


FIGURE 3.2: Schematic representation of pulse sequence for homonuclear polarization transfer experiment (HORROR experiments). The system consists of dipolar coupled homonuclear spins I_i . Polarization is transferred from one spin to other spin during the mixing time depicted between the two 90° Y pulses in the I channel.

chemical shift anisotropic part

$$H_{CSA}(t) = \sum_{i=1}^N \omega_i^m e^{im\omega_r t} I_{iz} \quad (3.16)$$

homonuclear dipolar coupling given by

$$H_D(t) = \sum_{i,j,i \neq j} \omega_{ij} \{2I_{iz}I_{jz} - (I_{ix}I_{jx} + I_{iy}I_{jy})\} e^{im\omega_r t} \quad (3.17)$$

and the RF interaction

$$H_{RF} = -\omega_{rf} \sum_{i=1}^N I_{ix} \quad (3.18)$$

In equation(4.3) resonance offset, Ω_i , ($i = 1, 2, \dots, N$), are given by the difference of the isotropic chemical shift and the Zeeman interaction. Resonance offset goes to zero in an on-resonance Zeeman frame.

$$\Omega_i = 0 \quad (3.19)$$

The effect of CSA is negligible compared to other parts of the Hamiltonian. In usual broad band dipolar experiments the amplitudes of the RF fields, ω_{rf} , are

much higher than CSA

$$\omega_{rf} \gg \omega_i^m \quad (3.20)$$

Therefore CSA is approximated to zero. $\omega_{ij}, i \neq j$ are the dipolar coupling constant between spin i and j . The time dependent parts of the Hamiltonian oscillate at ω_r and $2\omega_r$ because m can have values from -2 to $+2$ but $m \neq 0$. Thus the Hamiltonian in the on-resonance Zeeman Frame contains the dipolar and the RF frame.

$$H(t) = \sum_{i,j,i \neq j} \omega_{ij} \{2I_{iz}I_{jz} - (I_{ix}I_{jx} + I_{iy}I_{jy})\} e^{im\omega_r t} - \omega_{rf} \sum_{i=1}^N I_{ix} \quad (3.21)$$

The Hamiltonian is transformed in to a 90° tilted frame along Y axis using the the unitary transformation $H^T = U^\dagger H U$ where $U = e^{-i\frac{\pi}{2} \sum_{i=1}^N I_{iy}}$, so that we have the dominant RF interaction is along Z axis.

$$H^T(t) = \omega_{rf} \sum_{i=1}^N I_{iz} + \sum_{i,j,i \neq j} \omega_{ij} \{2I_{ix}I_{jx} - (I_{iz}I_{jz} + I_{iy}I_{jy})\} e^{im\omega_r t} \quad (3.22)$$

Homonuclear dipolar interaction can be decomposed in to DQ and ZQ operators.

$$H^T(t) = \omega_{rf} \sum_{i=1}^N I_{iz} + \sum_{i,j,i \neq j} \omega_{ij} \left\{ \frac{3}{4} (I_i^+ I_j^+ + I_i^- I_j^-) + \frac{1}{4} (I_i^+ I_j^- + I_i^- I_j^+) - I_{iz} I_{jz} \right\} e^{im\omega_r t} \quad (3.23)$$

Transforming to the RF interaction frame will isolate the recoupling condition the system and finds the time independent effective Hamiltonian. The transformation $\tilde{H}^T = U^\dagger H^T U$ is done by the unitary operator $U = e^{-i\omega_{rf} t \sum_{i=1}^N I_{iz}}$

$$\tilde{H}^T = \sum_{i,j,i \neq j} \omega_{ij} \left\{ \frac{3}{4} (I_i^+ I_j^+ e^{-i2\omega_{rf} t} + I_i^- I_j^- e^{i2\omega_{rf} t}) + \frac{1}{4} (I_i^+ I_j^- + I_i^- I_j^+) - I_{iz} I_{jz} \right\} e^{im\omega_r t} \quad (3.24)$$

The Hamiltonian becomes time dependent when

$$2\omega_{rf} = m\omega_r \quad (3.25)$$

$$m = \pm 2, \pm 1$$

Recoupling in homonuclear spin systems occurs in DQ term with effective dipolar coupling constant is three by fourth of dipolar coupling between spin i and spin j .

$$C_{ij} = \frac{3}{4}\omega_{ij} \quad (3.26)$$

$$H_{eff} = \sum_{i,j,i \neq j} C_{ij}(I_i^+ I_j^+ + I_i^- I_j^-) \quad (3.27)$$

Considering a two spin homonuclear spin system consisting of spins I_1 and I_2 The time independent effective Hamiltonian is given by the DQ operator

$$H_{eff} = C_d(I_1^+ I_2^+ + I_1^- I_2^-) \quad (3.28)$$

with effective dipolar coupling $C_d = \frac{3}{4}\omega_d$ where ω_d is the dipolar coupling constant. The Effective Hamiltonian in equation (4.15) is same as equation(3.13) that is effective Hamiltonian for heteronuclear two spin DQ polarization transfer.

3.2.1 ZQ Polarization Transfer, ($\omega_{1I} = \omega_{1S}$)

ZQ recoupling occurs when the on both the channels RF are set to the Hartmann-Hahn conditions $\omega_{1I} = \omega_{1S}$. As described above, in the case of ZQ experiments the effective Hamiltonian during the dipolar mixing time period in the RF interaction frame comprises of ZQ operator

$$H_{eff} = C_d(I_+ S_- + I_- S_+) \quad (3.29)$$

The evolution of the system under the effective hamiltonian (section 3.1) follows the QL Theorem. The state of the system at time, t , is given by

$$\rho(t) = e^{-iH_{eff}t} \rho(0) e^{iH_{eff}t} \quad (3.30)$$

The density operator under the effective Hamiltonian is derived using the BCH expansion

$$\rho(t) = \rho(0) + (-it)[H_{eff}, \rho(0)] + \frac{1}{2!}(-it)^2[H_{eff}, [H_{eff}, \rho(0)]] + \frac{1}{3!}(-it)^3[H_{eff}, [H_{eff}, [H_{eff}, \rho(0)]]] + \dots \quad (3.31)$$

The Static magnetic field(B_0) makes the spin's magnetic field align along the Z axis ie., the direction of B_0 . The 90° Y pulse in the I channel tilts the I spin magnetization to the X direction and in the tilted frame it is along Z direction. The state of the system can be described by the density operator. In the tilted frame the state of the system at time $t = 0$ is given by I_z operator.

$$\rho(0) = I_z \quad (3.32)$$

Thus the initial ($t = 0$) polarization in the I spin is along Z direction and there is no S spin polarization.

$$\langle I_z \rangle = 1 \quad (3.33)$$

$$\langle S_z \rangle = 0 \quad (3.34)$$

The system evolves under the ZQ Hamiltonian from the initial state $\rho(0) = I_z$ to the final state which can be decomposed to a ZQ operator, I_z operator and S_z operator

$$\rho(t) = I_z - i \frac{\sin(2C_d t)}{2} (I_- S_+ - I_+ S_-) - \sin^2(C_d t) (I_z - S_z) \quad (3.35)$$

From the above density operator the expectation value of angular momentum in different directions for the I spin and the S spin are estimated by trace of the product of operator and the density operator

$$\langle I_z \rangle = Trace(I_z \cdot \rho(t)) \quad (3.36)$$

$$\langle S_z \rangle = Trace(S_z \cdot \rho(t)) \quad (3.37)$$

Among the different parts of the density operator only the I_z and S_z operator contributes to the expectation values.

$$\langle I_z \rangle = 1 - \sin^2(C_d t) \quad (3.38)$$

$$\langle S_z \rangle = \sin^2(C_d t) \quad (3.39)$$

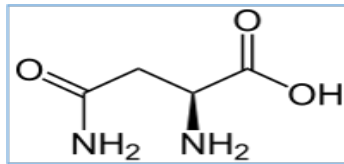


FIGURE 3.3: Asparagine Molecule

The Z magnetization of the I spin got reduced and there is an increase in that of the S spin. The increase in the magnetization of the S spin is equal to the decrease in the magnetization in the I spin. The magnetization in the I and the S spin are oscillating with a frequency that is half the dipolar coupling constant. The magnetization in the I spin reduced by $\sin^2(C_d t)$. Initially the magnetization was along I_z only. The polarization got transferred from the I spin to S spin.

As depicted in Equation(3.38) and Equation(3.39), the polarization transfer profile resembles to the Rabi Oscillations. This result is confirmed through numerical simulation depicted in FIGURE 3.4.

3.2.2 DQ Polarization Transfer, $(\omega_{1I} = -\omega_{1S})$

The effective Hamiltonian is $H_{eff} = C_d(I_+ S_+ + I_- S_-)$ when RF pulse in both channel are according to the Hartmann-Hahn matching condition $\omega_{1I} = -\omega_{1S}$.

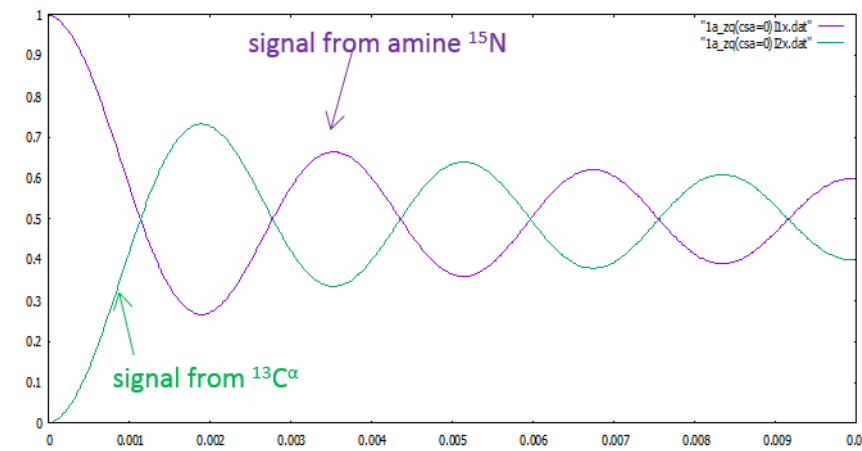


FIGURE 3.4: numerical simulation by SIMPSON for ZQ polarization transfer in heteronuclear spin system: The figure shows the polarization transfer from ^{15}N to ^{13}C in Asparagine. The polarization in the ^{15}N starts from the maximum and there is no Z magnetization in the S spin. Gradually the S spin magnetization increases along with a decrease in the I spin magnetization. The magnetization in the I and S spin are oscillating with a frequency that is half the dipolar coupling constant.

Initial state of the system, $\rho(0) = I_z$ evolve under the DQ effective Hamiltonian to a density operator which has a DQ, I_z and S_z parts.

$$\rho(t) = I_z - \frac{i}{2} \sin(2C_d t)(I_- S_- - I_+ S_+) - \sin^2(C_d t)(I_z + S_z) \quad (3.40)$$

The angular momentum Z component terms in the above equation contributes to the magnetization of both spins.

$$\langle I_z \rangle = 1 - \sin^2(C_d t) \quad (3.41)$$

$$\langle S_z \rangle = -\sin^2(C_d t) \quad (3.42)$$

The I spin Magnetization begin with the maximum value whereas the S spin started with zero magnetization. The magnetization gained by the S spin is equal to the the change in magnetization in I spin. The gain in the S spin magnetization is negative due π phase change. Thus the gain is due to DQ polarization transfer.

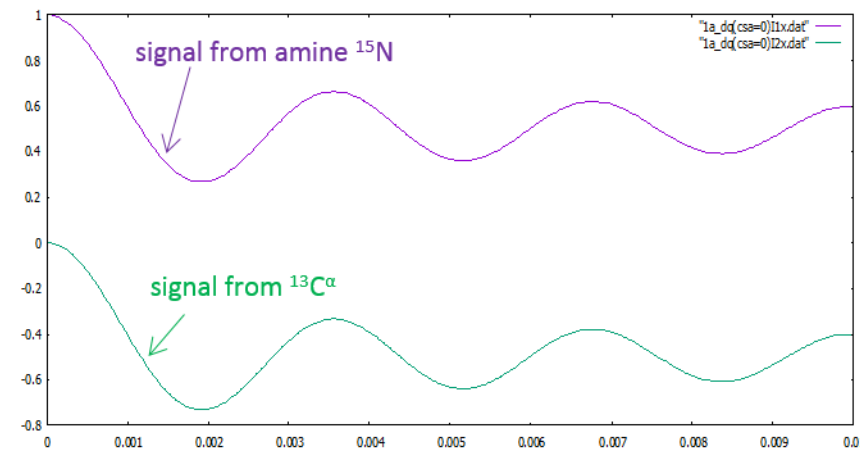


FIGURE 3.5: numerical simulation by SIPMSON for DQ polarization transfer in heteronuclear spin system: The figure shows the polarization transfer from ^{15}N to ^{13}C in Asparagine. The polarization in the ^{15}N starts from the maximum and there is no Z magnetization in the S spin. Gradually the S spin magnetization increases in the negative direction along with a decrease in the I spin magnetization. The magnetization in the I and S spin are oscillating with a frequency that is half the dipolar coupling constant

Initially the magnetization was along I_z only. The polarization got transferred from the I spin to S spin

3.2.3 Effect of RF interaction in Polarization Transfer

Under Hartmann-Hahn matching conditions the effective Hamiltonians does not depend on RF amplitudes. To know the effect of RF amplitudes, the effective Hamiltonian is chosen to be the Hamiltonian in the tilted frame (Equation(3.7)).

$$H_{eff} = \omega_{1I}I_z + \omega_{1S}S_z + C_d(I_+S_+ + I_-S_-) + C_d(I_+S_- + I_-S_+) \quad (3.43)$$

Hamiltonian before changing in to the RF interaction frame, depends the RF amplitude. The Hamiltonian has both ZQ and DQ as well as RF terms. The state of the system evolved under H_{eff} has the terms representing DQ and ZQ

recoupling

$$\begin{aligned}
 \rho(t) = & I_z - \frac{iC_d}{(4C_d^2 + (\omega_{1I} - \omega_{1S})^2)^{\frac{1}{2}}} (\sin((4C_d^2 + (\omega_{1I} - \omega_{1S})^2)^{\frac{1}{2}}t))(I_-S_+ - I_+S_-) \\
 & - \frac{iC_d}{(4C_d^2 + (\omega_{1I} + \omega_{1S})^2)^{\frac{1}{2}}} \sin((4C_d^2 + (\omega_{1I} + \omega_{1S})^2)^{\frac{1}{2}}t)(I_-S_- - I_+S_+) \\
 & + \frac{2C_d(\omega_{1I} - \omega_{1S})}{(4C_d^2 + (\omega_{1I} - \omega_{1S})^2)} \sin^2 \frac{(4C_d^2 + (\omega_{1I} - \omega_{1S})^2)^{\frac{1}{2}}t}{2} (I_+S_- + I_-S_+) \\
 & + \frac{2C_d(\omega_{1I} + \omega_{1S})}{(4C_d^2 + (\omega_{1I} + \omega_{1S})^2)} \sin^2 \frac{(4C_d^2 + (\omega_{1I} + \omega_{1S})^2)^{\frac{1}{2}}t}{2} (I_+S_+ + I_-S_-) \\
 & + \frac{4C_d^2}{(4C_d^2 + (\omega_{1I} - \omega_{1S})^2)} \sin^2 \frac{(4C_d^2 + (\omega_{1I} - \omega_{1S})^2)^{\frac{1}{2}}t}{2} (I_z - S_z) \\
 & + \frac{4C_d^2}{(4C_d^2 + (\omega_{1I} + \omega_{1S})^2)} \sin^2 \frac{(4C_d^2 + (\omega_{1I} + \omega_{1S})^2)^{\frac{1}{2}}t}{2} (I_z + S_z) \quad (3.44)
 \end{aligned}$$

The magnetization evolving under this Hamiltonian is given by the expectation value of S_z and I_z ,

$$\langle I_z \rangle = 1 - \frac{C_d^2}{C_d^2 + (\frac{\omega_{1I} - \omega_{1S}}{2})^2} \sin^2 \sqrt{C_d^2 + (\frac{\omega_{1I} - \omega_{1S}}{2})^2}t - \frac{C_d^2}{C_d^2 + (\frac{\omega_{1I} + \omega_{1S}}{2})^2} \sin^2 \sqrt{C_d^2 + (\frac{\omega_{1I} + \omega_{1S}}{2})^2}t \quad (3.45)$$

$$\langle S_z \rangle = \frac{C_d^2}{C_d^2 + (\frac{\omega_{1I} - \omega_{1S}}{2})^2} \sin^2 \sqrt{C_d^2 + (\frac{\omega_{1I} - \omega_{1S}}{2})^2}t - \frac{C_d^2}{C_d^2 + (\frac{\omega_{1I} + \omega_{1S}}{2})^2} \sin^2 \sqrt{C_d^2 + (\frac{\omega_{1I} + \omega_{1S}}{2})^2}t \quad (3.46)$$

Chapter 4

Polarization Transfer in Multi-spin Systems

The next stage in our study was to extend the calculations to a system comprising of strongly coupled spins. In a strongly coupled spin system, polarization transfer among spins takes place through a) band selective transfer b) Relay transfer c) both band selective and relay transfer. Here in this chapter, we make a modest attempt to describe the polyatomic transfer in a multi-spin system

4.1 Band Selective Polarization Transfer

In band selective experiments, polarization from a single spin (say I_1) is transferred to a group of spins $I_i, i = 1, 2, 3, \dots, N$ through dipolar interaction. All the spins are coupled to a single spin, I_1 , and no other couplings are there. Such interactions are quite common in both homonuclear and heteronuclear spin systems and are frequently employed in spectral—— experiments. Depending on the Experimental conditions both zero-quantum (ZQ) and double quantum (DQ) band selective transfer of polarization is possible. A brief description of this phenomenon is illustrated in the following section

4.1.1 ZQ Experiments

ZQ polarization as mentioned already happens only in heteronuclear spin systems. ZQ Band Selective polarization transfer happens when the RF amplitude in all the spins are equal. The Hamiltonian for this system in the doubly rotating frame is the sum of the ZQ operators for all spin with spin I_i .

$$H_{eff} = \sum_{i,j,i \neq j} C_{ij}(I_i^+ I_j^- + I_i^- I_j^+) \quad (4.1)$$

the Hamiltonian in Equation(5.1) causes polarization transfer from spin I_1 to other spins.

In this selection polarization transfer in a three spin heteronuclear spin, I_1 , I_2 and I_3 , is described. The Hamiltonian for this system is

$$H_{eff} = C_{12}(I_1^+ I_2^- + I_1^- I_2^+) + C_{13}(I_1^+ I_3^- + I_1^- I_3^+) \quad (4.2)$$

RF amplitudes of spin channels I_1 , I_2 and I_3 are equal, $\omega_{1I_1} = \omega_{1I_2} = \omega_{1I_3}$. the initial state of the system is assumed to be

$$\rho(0) = \frac{1}{2} I_{1z} \quad (4.3)$$

Hence at $t = 0$ only I_1 spin was polarized. The Z magnetization of I_2 and I_3 is zero

$$\langle I_{1z} \rangle = 1 \quad (4.4)$$

$$\langle I_{2z} \rangle = 0 \quad (4.5)$$

$$\langle I_{3z} \rangle = 0 \quad (4.6)$$

Due to the evolution under effective Hamiltonian in Equation(5.2) the state of the system at any time t is given by unitary transformation $\rho(t) = U^\dagger \rho(0) U$ where the

evolution operator $U = e^{-iH_{eff}t}$

$$\begin{aligned}
\rho(t) &= \frac{1}{2}I_{1z} - \frac{iC_{12}}{4(C_{12}^2 + C_{13}^2)^{\frac{1}{2}}} \sin(2(C_{12}^2 + C_{13}^2)^{\frac{1}{2}}t)(I_1^- I_2^+ - I_1^+ I_2^-) \\
&- \frac{iC_{13}}{4(C_{12}^2 + C_{13}^2)^{\frac{1}{2}}} \sin(2(C_{12}^2 + C_{13}^2)^{\frac{1}{2}}t)(I_1^- I_3^+ - I_1^+ I_3^-) \\
&- \frac{C_{12}^2}{2(C_{12}^2 + C_{13}^2)} \sin^2((C_{12}^2 + C_{13}^2)^{\frac{1}{2}}t)(I_{1z} - I_{2z}) \\
&- \frac{C_{13}^2}{2(C_{12}^2 + C_{13}^2)} \sin^2((C_{12}^2 + C_{13}^2)^{\frac{1}{2}}t)(I_{1z} - I_{3z}) \\
&- \frac{C_{12}C_{13}}{2(C_{12}^2 + C_{13}^2)} \sin^2((C_{12}^2 + C_{13}^2)^{\frac{1}{2}}t) \\
&\times \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \tag{4.7}
\end{aligned}$$

The polarization in different spins changes during the pulse. Polarization in spin I_1 decreased by $\sin^2((C_{12}^2 + C_{13}^2)^{\frac{1}{2}}t)$ and that of spin I_2 and I_3 increased in proportion to its coupling constant with I_1 .

$$\langle I_{1z} \rangle = 1 - \sin^2((C_{12}^2 + C_{13}^2)^{\frac{1}{2}}t) \tag{4.8}$$

$$\langle I_{2z} \rangle = \frac{C_{12}^2}{(C_{12}^2 + C_{13}^2)} \sin^2((C_{12}^2 + C_{13}^2)^{\frac{1}{2}}t) \tag{4.9}$$

$$\langle I_{3z} \rangle = \frac{C_{13}^2}{(C_{12}^2 + C_{13}^2)} \sin^2((C_{12}^2 + C_{13}^2)^{\frac{1}{2}}t) \tag{4.10}$$

Polarization in each spin is a \sin^2 function with frequency of oscillation given by the square root of sum of squares of the dipolar coupling constant. The intensity of

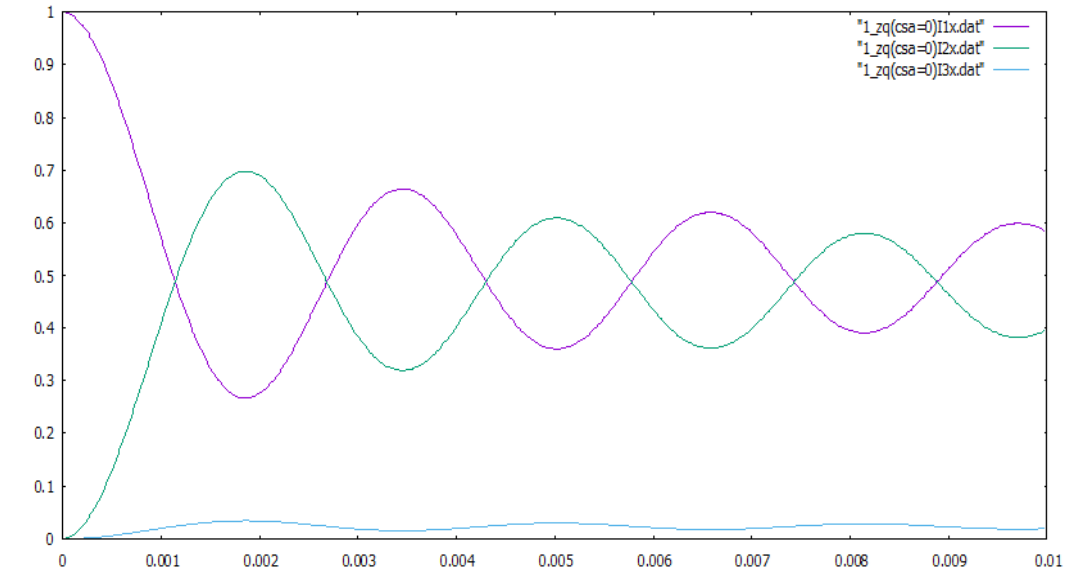


FIGURE 4.1: schematic representation of ZQ band selective polarization transfer from asparagine ^{15}N to $^{13}\text{C}^\alpha$ and $^{13}\text{C}^\beta$

polarization transfer is directly proportional to the square of the dipolar coupling and also it depends inversely sum squares of all the dipolar coupling constant. The reduction in the polarization of I_1 spin is sum of polarization transferred to both the spins.

Polarization transfer in FIGURE 5.1 shows the ZQ band selective polarization transfer from amine ^{15}N to $^{13}\text{C}^\alpha$ and $^{13}\text{C}^\beta$ in Asparagine molecule FIGURE 3.2. The dipolar constant for the $^{15}\text{N} - ^{13}\text{C}^\alpha$ is almost four times the dipolar constant for $^{15}\text{N} - ^{13}\text{C}^\beta$

. Therefore the transfer to $^{13}\text{C}^\alpha$ is 16 times the transfer to $^{13}\text{C}^\beta$.

The polarization transfer to each spin is dependent on the transfer to other spin. When one of the coupling constant is very high the polarization transfer to the other spin reduces considerably. In the spin system I_1 , I_2 and I_3 , if $C_{12} \gg C_{13}$, $C_{12} + C_{13} \cong C_{12}$ thus polarization is given by

$$\langle I_{1z} \rangle = 1 - \sin^2 C_{12}t \quad (4.11)$$

$$\langle I_{2z} \rangle = \sin^2 C_{12}t \quad (4.12)$$

$$\langle I_{3z} \rangle = \frac{C_{13}^2}{C_{12}^2} \sin^2 C_{12}t \quad (4.13)$$

When the magnitude of one of the dipolar coupling exceeds the other pair, polarization transfer from the first spin pair is reduced (or truncated) due to the presence of the stronger coupling between the second pair. This phenomenon is termed as **Dipolar Truncation** and is substituted through both analytic theory and numerical simulation.

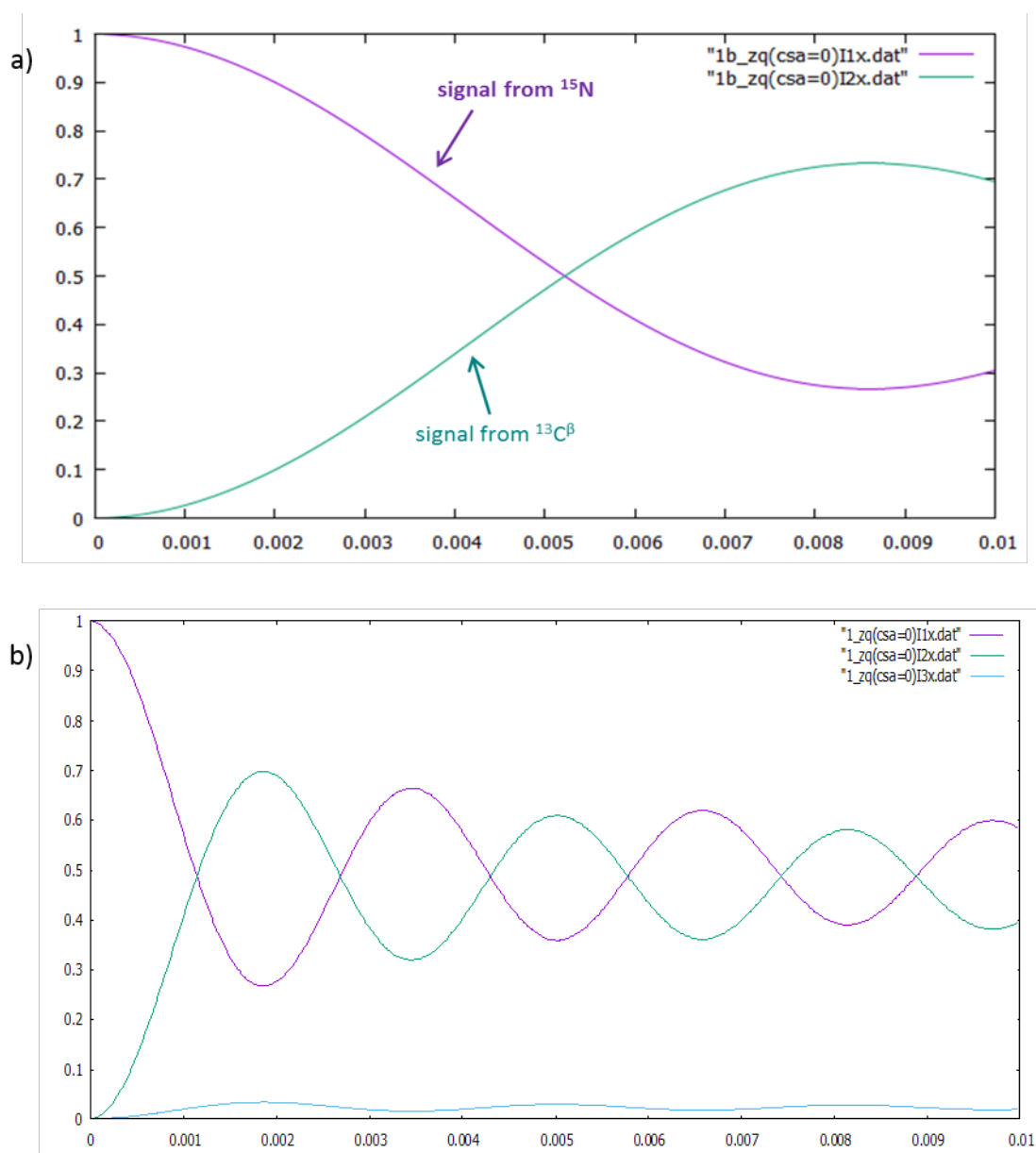


FIGURE 4.2: schematic representation of ZQ dipolar truncation: a) band selective polarization transfer from asparagine ^{15}N to $^{13}\text{C}\beta$ b) truncation of polarization transfer to $^{13}\text{C}\beta$ due to introduction of $^{13}\text{C}\alpha$

FIGURE 5.2a shows polarization transfer from ^{15}N to $^{13}\text{C}^\beta$. The polarization transfer obeys Equation(3.24) which has an intensity of 1. But when a more stronger coupling is introduced say $^{13}\text{C}^\alpha$ the polarization transfer to $^{13}\text{C}^\beta$ reduced to almost $\frac{1}{17}$.

Extending the above calculation to a model four spin system the effective Hamiltonian describing the polarization transfer is represented below

$$H_{eff} = C_{12}(I_1^+ I_2^- + I_1^- I_2^+) + C_{13}(I_1^+ I_3^- + I_1^- I_3^+) + C_{14}(I_1^+ I_4^- + I_1^- I_4^+) \quad (4.14)$$

Accordingly, the polarization transfer from spin I_1 to the remaining spins are described through the following equations

$$\langle I_{1z} \rangle = 1 - \sin^2((C_{12}^2 + C_{13}^2 + C_{14}^2)^{\frac{1}{2}} t) \quad (4.15)$$

$$\langle I_{2z} \rangle = \frac{C_{12}^2}{(C_{12}^2 + C_{13}^2 + C_{14}^2)} \sin^2((C_{12}^2 + C_{13}^2 + C_{14}^2)^{\frac{1}{2}} t) \quad (4.16)$$

$$\langle I_{3z} \rangle = \frac{C_{13}^2}{(C_{12}^2 + C_{13}^2 + C_{14}^2)} \sin^2((C_{12}^2 + C_{13}^2 + C_{14}^2)^{\frac{1}{2}} t) \quad (4.17)$$

$$\langle I_{4z} \rangle = \frac{C_{14}^2}{(C_{12}^2 + C_{13}^2 + C_{14}^2)} \sin^2((C_{12}^2 + C_{13}^2 + C_{14}^2)^{\frac{1}{2}} t) \quad (4.18)$$

Based on the present study, the calculations to N -spin is described through the following equation

$$H_{eff} = \sum_{i=2}^N C_{1i}(I_1^+ I_i^- + I_1^- I_i^+) \quad (4.19)$$

$$\rho(0) = \frac{1}{2^{N-2}} I_{1z} \quad (4.20)$$

The expectation value of angular momentum along different directions are given by

$$\langle I_{1z} \rangle = 1 - \sin^2((\sum_{i=2}^N C_{1i}^2)^{\frac{1}{2}} t) \quad (4.21)$$

$$\langle I_{iz} \rangle = \frac{C_{1i}^2}{\sum_{i=2}^N C_{1i}^2} \sin^2\left(\left(\sum_{i=2}^N C_{1i}^2\right)^{\frac{1}{2}} t\right) \quad (4.22)$$

4.1.2 DQ Experiments

DQ polarization transfer happens in both heteronuclear as well as homonuclear nuclear spin systems. The Hamiltonian for this system in the doubly rotating frame is the sum of the DQ operators.

$$H_{eff} = \sum_{i=2}^N C_{ij} (I_i^+ I_j^+ + I_i^- I_j^-) \quad (4.23)$$

This Hamiltonian causes polarization transfer from I_1 to all other spin. The RF pulse amplitude in all the spins are negative of that in I_1 . The Hamiltonian for DQ Band selective polarization transfer in a three spin heteronuclear spin, I_1 , I_2 and I_3 , is described as

$$H_{eff} = C_{12} (I_1^+ I_2^+ + I_1^- I_2^-) + C_{13} (I_1^+ I_3^+ + I_1^- I_3^-) \quad (4.24)$$

State of the system at $t = 0$ is given by Equation(5.3) and that during the pulse is

$$\begin{aligned} \rho(t) &= \frac{1}{2} I_{1z} - \frac{iC_{12}}{4(C_{12}^2 + C_{13}^2)^{\frac{1}{2}}} \sin(2(C_{12}^2 + C_{13}^2)^{\frac{1}{2}} t) (I_1^- I_2^- - I_1^+ I_2^+) \\ &- \frac{iC_{13}}{4(C_{12}^2 + C_{13}^2)^{\frac{1}{2}}} \sin(2(C_{12}^2 + C_{13}^2)^{\frac{1}{2}} t) (I_1^- I_3^- - I_1^+ I_3^+) \\ &- \frac{C_{12}^2}{2(C_{12}^2 + C_{13}^2)} \sin^2((C_{12}^2 + C_{13}^2)^{\frac{1}{2}} t) (I_{1z} + I_{2z}) \\ &- \frac{C_{13}^2}{2(C_{12}^2 + C_{13}^2)} \sin^2((C_{12}^2 + C_{13}^2)^{\frac{1}{2}} t) (I_{1z} + I_{3z}) \\ &- \frac{C_{12} C_{13}}{2(C_{12}^2 + C_{13}^2)} \sin^2((C_{12}^2 + C_{13}^2)^{\frac{1}{2}} t) \end{aligned}$$

$$\times \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (4.25)$$

Polarization in both the spins I_2 and I_3 increased from zero to an oscillating modulated function but there is a phase change of π , making the polarization in these spins to be negative.

$$\langle I_{1z} \rangle = 1 - \sin^2((C_{12}^2 + C_{13}^2)^{\frac{1}{2}}t) \quad (4.26)$$

$$\langle I_{2z} \rangle = \frac{-C_{12}^2}{(C_{12}^2 + C_{13}^2)} \sin^2((C_{12}^2 + C_{13}^2)^{\frac{1}{2}}t) \quad (4.27)$$

$$\langle I_{3z} \rangle = \frac{-C_{13}^2}{(C_{12}^2 + C_{13}^2)} \sin^2((C_{12}^2 + C_{13}^2)^{\frac{1}{2}}t) \quad (4.28)$$

Similar to the case in ZQ, polarization in each spin is a modulated function with frequency of oscillation given by the square root of sum of squares of the dipolar coupling constant. The intensity of polarization transfer is directly proportional to the square of the dipolar coupling and also it depends inversely sum squares of all the dipolar coupling constant. The reduction in the polarization of I_1 spin is sum of polarization transferred to both the spins.

Dependence of polarization transfer on other couplings involved in the system is there in the DQ band selective transfer also like in case of ZQ. As the dipolar constant between I_1 and I_2 is much greater than that between I_1 and I_3 , the transfer approaches the transfer in a two spin system

$$\langle I_{1z} \rangle = 1 - \sin^2 C_{12}t \quad (4.29)$$

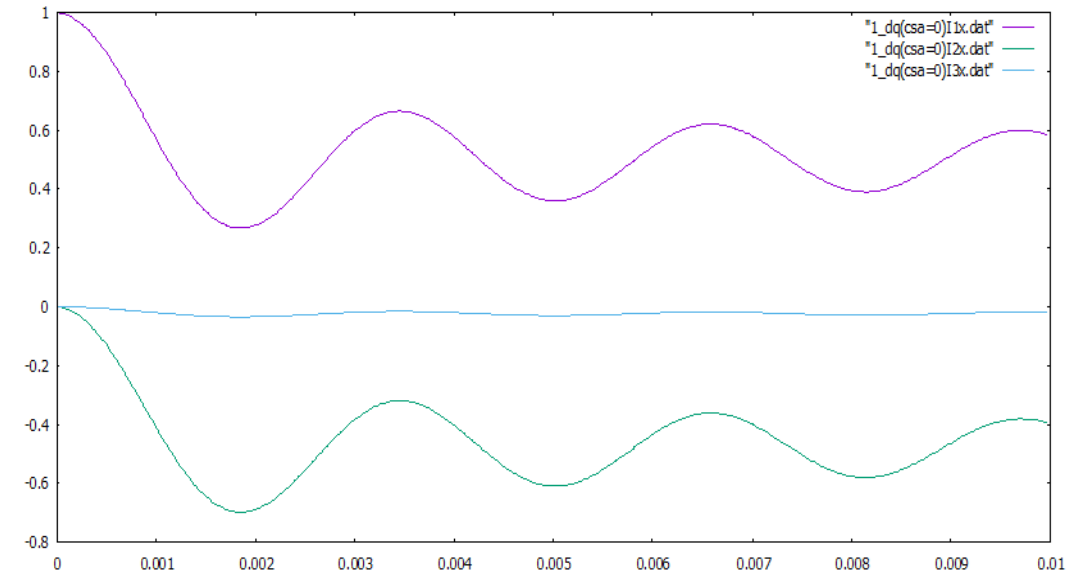


FIGURE 4.3: schematic representation of DQ band selective polarization transfer from asparagine ^{15}N to $^{13}C^{\alpha}$ and $^{13}C^{\beta}$

$$\langle I_{2z} \rangle = -\sin^2 C_{12}t \quad (4.30)$$

$$\langle I_{3z} \rangle = \frac{-C_{13}^2}{C_{12}^2} \sin^2 C_{12}t \quad (4.31)$$

As the coupling to second spin increases the transfer to third spin goes to zero.

Due higher dipolar constant between ^{15}N and $^{13}C^{\alpha}$ the initial transfer to $^{13}C^{\alpha}$ (FIGURE5.4a) reduces to zero (FIGURE5.4b).

Extending the above to four spin system the time independent effective Hamiltonian is

$$H_{eff} = C_{12}(I_1^+ I_2^+ + I_1^- I_2^-) + C_{13}(I_1^+ I_3^+ + I_1^- I_3^-) + C_{14}(I_1^+ I_4^+ + I_1^- I_4^-) \quad (4.32)$$

The polarization transfer from I_1 to remaining spins is described by

$$\langle I_{1z} \rangle = 1 - \sin^2((C_{12}^2 + C_{13}^2 + C_{14}^2)^{\frac{1}{2}}t) \quad (4.33)$$

$$\langle I_{2z} \rangle = \frac{-C_{12}^2}{(C_{12}^2 + C_{13}^2 + C_{14}^2)} \sin^2((C_{12}^2 + C_{13}^2 + C_{14}^2)^{\frac{1}{2}}t) \quad (4.34)$$

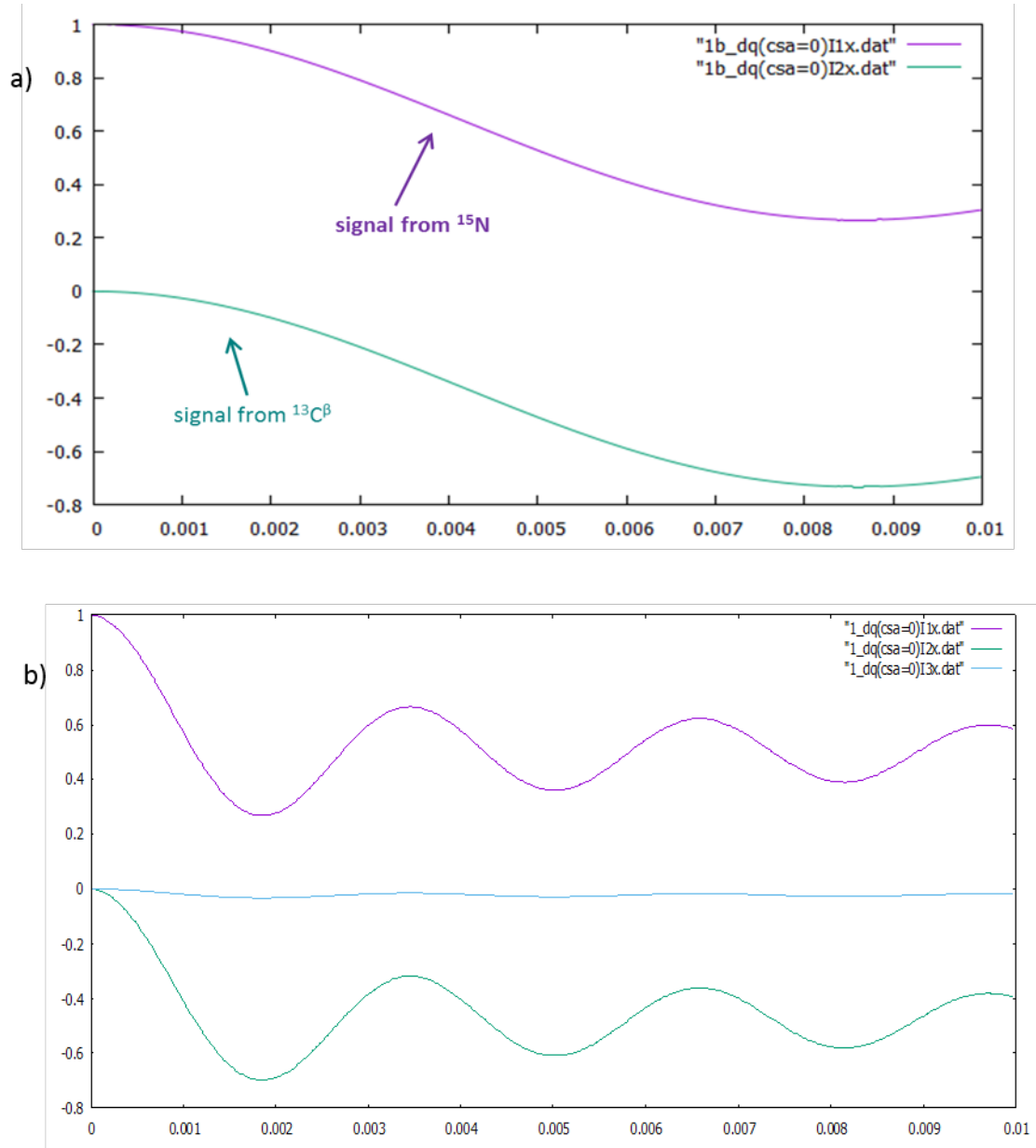


FIGURE 4.4: schematic representation of DQ dipolar truncation:a) band selective polarization transfer from asparagine ^{15}N to $^{13}\text{C}^\beta$ b) truncation of polarization transfer to $^{13}\text{C}^\beta$ due to introduction of $^{13}\text{C}^\alpha$

$$\langle I_{3z} \rangle = \frac{-C_{13}^2}{(C_{12}^2 + C_{13}^2 + C_{14}^2)} \sin^2((C_{12}^2 + C_{13}^2 + C_{14}^2)^{\frac{1}{2}} t) \quad (4.35)$$

$$\langle I_{4z} \rangle = \frac{-C_{14}^2}{(C_{12}^2 + C_{13}^2 + C_{14}^2)} \sin^2((C_{12}^2 + C_{13}^2 + C_{14}^2)^{\frac{1}{2}} t) \quad (4.36)$$

Based on the study in Section(5.1.2) the expressions for N spin systems are

$$H_{eff} = \sum_{i=2}^N C_{1i} (I_1^+ I_i^+ + I_1^- I_i^-) \quad (4.37)$$

$$\rho(0) = \frac{1}{2^{N-2}} I_{1z} \quad (4.38)$$

The expectation value of angular momentum along different directions are given by

$$\langle I_{1z} \rangle = 1 - \sin^2\left(\left(\sum_{i=2}^N C_{1i}^2\right)^{\frac{1}{2}} t\right) \quad (4.39)$$

$$\langle I_{iz} \rangle = \frac{-C_{1i}^2}{\sum_{i=2}^N C_{1i}^2} \sin^2\left(\left(\sum_{i=2}^N C_{1i}^2\right)^{\frac{1}{2}} t\right) \quad (4.40)$$

4.2 Relayed Polarization Transfer

In systems where both stronger and weaker coupling exist, direct transfer of polarization between spins that are spatially apart is less efficient. In such cases, polarization transfer takes place through intermediate couplings. Such transfer of polarization is termed as Relayed Transfer of polarization in NMR. Employing a model three spin system, an analytic description of relayed transfer is presented in the following sections

4.2.1 ZQ Experiments

Let us consider a model three spin system, where the coupling between I_1 and I_3 are weak and ignored in the present discussion. In an appropriate interaction frame, the effective Hamiltonian describing such a system is represented below

$$H_{eff} = C_{12}(I_1^+ I_2^- + I_1^- I_2^+) + C_{13}(I_2^+ I_3^- + I_2^- I_3^+) \quad (4.41)$$

$$\rho(0) = \frac{1}{2} I_{1z} \quad (4.42)$$

$$\begin{aligned}
\rho(t) = & \frac{1}{2}I_{1z} + \left\{ \frac{-iC_{12}}{4(C_{12}^2 + C_{23}^2)^{\frac{1}{2}}} \sin(2(C_{12}^2 + C_{23}^2)^{\frac{1}{2}}t) \right. \\
& - \frac{iC_{12}C_{23}^2}{(C_{12}^2 + C_{23}^2)^{\frac{3}{2}}} \sin((C_{12}^2 + C_{23}^2)^{\frac{1}{2}}t) \sin^2\left(\frac{(C_{12}^2 + C_{23}^2)^{\frac{1}{2}}}{2}t\right) \left. \right\} (I_1^- I_2^+ - I_1^+ I_2^-) \\
& + \frac{iC_{12}^2 C_{23}}{(C_{12}^2 + C_{23}^2)^{\frac{3}{2}}} \sin((C_{12}^2 + C_{23}^2)^{\frac{1}{2}}t) \sin^2\left(\frac{(C_{12}^2 + C_{23}^2)^{\frac{1}{2}}}{2}t\right) \left. \right\} (I_2^+ I_3^- - I_2^- I_3^+) \\
& - \left\{ \frac{C_{12}^2}{2(C_{12}^2 + C_{23}^2)} \sin^2((C_{12}^2 + C_{23}^2)^{\frac{1}{2}}t) - \frac{C_{12}^2 C_{23}^2}{2(C_{12}^2 + C_{23}^2)^2} \sin^4\left(\frac{(C_{12}^2 + C_{23}^2)^{\frac{1}{2}}}{2}t\right) \right\} (I_{1z} - I_{2z}) \\
& + \frac{C_{12}^2 C_{23}^2}{2(C_{12}^2 + C_{23}^2)^2} \sin^4\left(\frac{(C_{12}^2 + C_{23}^2)^{\frac{1}{2}}}{2}t\right) \left. \right\} (I_{3z} - I_{2z}) \\
& - \left\{ \frac{C_{12} C_{23}}{4(C_{12}^2 + C_{23}^2)} \sin^2((C_{12}^2 + C_{23}^2)^{\frac{1}{2}}t) + \frac{C_{12} C_{23} (C_{12}^2 - C_{23}^2)}{(C_{12}^2 + C_{23}^2)} \sin^4\left(\frac{(C_{12}^2 + C_{23}^2)^{\frac{1}{2}}}{2}t\right) \right\} \\
& \times \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \tag{4.43}
\end{aligned}$$

Expectation values of angular momentum in different directions

$$\langle I_{1z} \rangle = 1 - \frac{C_{12}^2}{2(C_{12}^2 + C_{23}^2)} \sin^2((C_{12}^2 + C_{23}^2)^{\frac{1}{2}}t) - \frac{C_{12}^2 C_{23}^2}{2(C_{12}^2 + C_{23}^2)^2} \sin^4\left(\frac{(C_{12}^2 + C_{23}^2)^{\frac{1}{2}}}{2}t\right) \tag{4.44}$$

$$\langle I_{2z} \rangle = \frac{C_{12}^2}{2(C_{12}^2 + C_{23}^2)} \sin^2((C_{12}^2 + C_{23}^2)^{\frac{1}{2}}t) \tag{4.45}$$

$$\langle I_{3z} \rangle = \frac{C_{12}^2 C_{23}^2}{2(C_{12}^2 + C_{23}^2)^2} \sin^4\left(\frac{(C_{12}^2 + C_{23}^2)^{\frac{1}{2}}}{2}t\right) \tag{4.46}$$

Although, no direct coupling between spin I_1 and I_3 exist, the expectation value or polarization transfer to spin I_3 is non-zero. The simulation validate the above analytic expressions. Hence, in a strongly coupled spin network, indirect transfer of polarization is always possible.

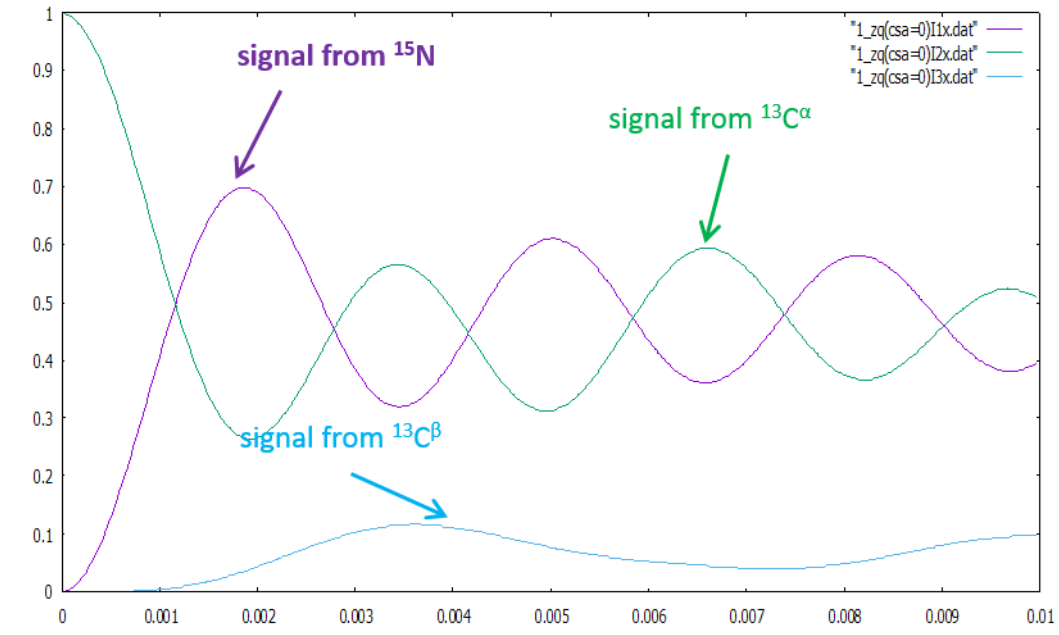


FIGURE 4.5: Schematic depiction of ZQ Relay polarization transfer from $^{13}\text{C}^\alpha$ to $^{13}\text{C}^\beta$ through ^{15}N in Asparagine molecule

4.2.2 DQ Experiments

Analogous to the description presented in the ZQ experiments, a model Hamiltonian comprising of two dipolar coupling constants is employed for describing relayed transfer of polarization

$$H_{eff} = C_{12}(I_1^+ I_2^+ + I_1^- I_2^-) + C_{13}(I_2^+ I_3^+ + I_2^- I_3^-) \quad (4.47)$$

$$\rho(0) = \frac{1}{2} I_{1z} \quad (4.48)$$

$$\begin{aligned}
\rho(t) = & \frac{1}{2}I_{1z} + \left\{ \frac{-iC_{12}}{4(C_{12}^2 + C_{23}^2)^{\frac{1}{2}}} \sin(2(C_{12}^2 + C_{23}^2)^{\frac{1}{2}}t) \right. \\
& - \frac{iC_{12}C_{23}^2}{(C_{12}^2 + C_{23}^2)^{\frac{3}{2}}} \sin((C_{12}^2 + C_{23}^2)^{\frac{1}{2}}t) \sin^2\left(\frac{(C_{12}^2 + C_{23}^2)^{\frac{1}{2}}}{2}t\right) \left. \right\} (I_1^- I_2^- - I_1^+ I_2^+) \\
& + \frac{iC_{12}^2 C_{23}}{(C_{12}^2 + C_{23}^2)^{\frac{3}{2}}} \sin((C_{12}^2 + C_{23}^2)^{\frac{1}{2}}t) \sin^2\left(\frac{(C_{12}^2 + C_{23}^2)^{\frac{1}{2}}}{2}t\right) \left. \right\} (I_2^- I_3^- - I_2^+ I_3^+) \\
& - \left\{ \frac{C_{12}^2}{2(C_{12}^2 + C_{23}^2)} \sin^2((C_{12}^2 + C_{23}^2)^{\frac{1}{2}}t) - \frac{C_{12}^2 C_{23}^2}{2(C_{12}^2 + C_{23}^2)^2} \sin^4\left(\frac{(C_{12}^2 + C_{23}^2)^{\frac{1}{2}}}{2}t\right) \right\} (I_{1z} + I_{2z}) \\
& + \frac{C_{12}^2 C_{23}^2}{2(C_{12}^2 + C_{23}^2)^2} \sin^4\left(\frac{(C_{12}^2 + C_{23}^2)^{\frac{1}{2}}}{2}t\right) \left. \right\} (I_{3z} + I_{2z}) \\
& - \left\{ \frac{C_{12} C_{23}}{4(C_{12}^2 + C_{23}^2)} \sin^2((C_{12}^2 + C_{23}^2)^{\frac{1}{2}}t) + \frac{C_{12} C_{23} (C_{12}^2 - C_{23}^2)}{(C_{12}^2 + C_{23}^2)} \sin^4\left(\frac{(C_{12}^2 + C_{23}^2)^{\frac{1}{2}}}{2}t\right) \right\}
\end{aligned}$$

$$\times \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (4.49)$$

Expectation values of angular momentum in different directions

$$\langle I_{1z} \rangle = 1 - \frac{C_{12}^2}{2(C_{12}^2 + C_{23}^2)} \sin^2((C_{12}^2 + C_{23}^2)^{\frac{1}{2}}t) - \frac{C_{12}^2 C_{23}^2}{2(C_{12}^2 + C_{23}^2)^2} \sin^4\left(\frac{(C_{12}^2 + C_{23}^2)^{\frac{1}{2}}}{2}t\right) \quad (4.50)$$

$$\langle I_{2z} \rangle = \frac{-C_{12}^2}{2(C_{12}^2 + C_{23}^2)} \sin^2((C_{12}^2 + C_{23}^2)^{\frac{1}{2}}t) \quad (4.51)$$

$$\langle I_{3z} \rangle = \frac{C_{12}^2 C_{23}^2}{2(C_{12}^2 + C_{23}^2)^2} \sin^4\left(\frac{(C_{12}^2 + C_{23}^2)^{\frac{1}{2}}}{2}t\right) \quad (4.52)$$

In contrast to Polarization transfer in ZQ Experiments the sign of polarization transfer differ in DQ experiment. In DQ experiments involving direct transfer of polarization the polarization transfer profile has a negative sign. By contrast, in

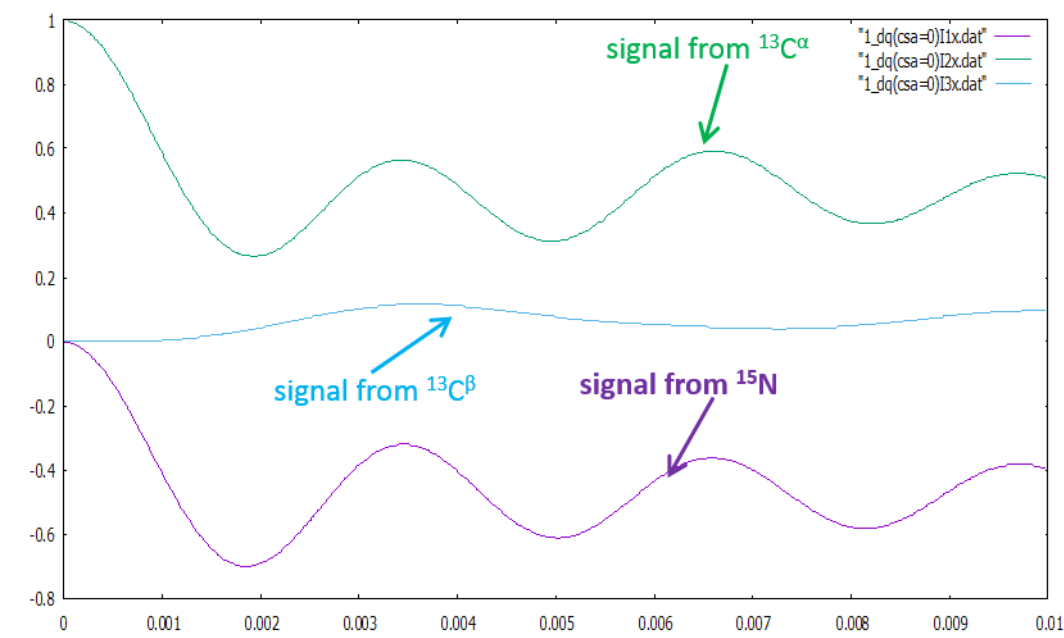


FIGURE 4.6: Schematic depiction of DQ Relay polarization transfer from $^{13}\text{C}^\alpha$ to $^{13}\text{C}^\beta$ through ^{15}N in Asparagine molecule

cases of indirect transfer, the polarization transfer has positive sign. This prediction emerging from the analytic theory is well substituted in the numerical simulations depicted.

4.3 Conclusion and Perspectives

In summary, the model Hamiltonians employed for describing band selective and relayed transfer presents an attractive framework for quantifying polarization transfer in multi-spin systems. The model Hamiltonians employed in the thesis resembles to those employed in Solid state NMR experiments and the analytic expressions presented could be employed for quantifying distance measurement experiments in SSNMR. The description presented in this thesis could be extended for quantifying polarization transfer in strongly coupled network of spins in solids

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