Theory of Selective and Non-selective Excitations in Magnetic Resonance

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Certificate of Examination

This is to certify that the dissertation titled "**Theory of Selective and Non-selective Excitations in Magnetic Resonance**" submitted by **Mr. Dharmendra Kumar Singh** (Reg. No. MS07010) for the partial fulfillment 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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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.

Dharmendra Kumar singh
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Dated: May 4, 2012

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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Dharmendra Kumar Singh

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Notations

μ	Nuclear magnetic moment;
I	Spin quantum number;
m	Spin magnetic quantum number;
$\hbar$	Planck's constant;
γ	Gyromagnetic ratio;
B_0	Applied external magnetic field;
E	Energy;
$\lvert I\ \mathrm{m}\rangle$	Ket Eigen basis;
I_Z , I_X , I_Y	Spin angular momentum operators;
I^+ , I^-	Lowering and Raising operators;
I^2	Identity operator;
ρ	Density matrix / operator;
ψ	Wave function;
Tr	Trace of matrix;
$\tilde{\sigma}$	Second rank tensor;
$\langle \hat{O}p \rangle$	Expectation value of corresponding observable;
k_B	Boltzmann constant;
T	absolute temperature;
t	time parameter;
i	iota;
RF	Oscillating magnetic field;
H	Hamiltonian;
H_Z	Zeeman Hamiltonian;
H_{RF}	RF interaction Hamiltonian;
H_J	Scalar coupling or J – coupling Hamiltonian;
H_D	Dipolar coupling Hamiltonian;
H_{CS}	Chemical shift interaction Hamiltonian;
H_Q	Quadrupolar interaction Hamiltonian;
$H_Q^{(1)}$	First order quadrupolar coupling;
$H_Q^{(2)}$	Second order quadrupolar coupling;

ω_Q	Quadrupolar coupling constant;
ω_0	Larmor frequency;
ω_1	Power of oscillating field;
ω_{rf}	Frequency of oscillating field;
d	Dipolar constant;
U	Unitary transformation;
$\Delta\omega$	Chemical shift;
$\tilde{H}$	Hamiltonian after first transformation;
$\tilde{\tilde{H}}$	Hamiltonian after second transformation;
$H_0^{(1)}, H_1^{(1)}, H_2^{(1)}$	Zeroth, 1st, 2nd, order Hamiltonians respectively, after first transformation;
$H_0^{(2)}, H_1^{(2)}, H_2^{(2)}$	Zeroth, 1st, 2nd, order Hamiltonians respectively, after second transformation.
$[A, B]$	Commutator of *A* and *B;*
CP	Cross-polarization;
CT	Contact transformation;
^{1}H	Proton;
^{13}C	NMR active carbon isotope with spin-1/2;
DQ	Double quantum;
ZQ	Zero quantum;
$\rho(0)$	Initial density operator;
$\rho(t)$	Evolved density operator;
MHz	Mega Hertz;
kHz	Kilo Hertz;
PAS	Principle Axis System;
LAS	Lab Axis System;
BCH	Baker Campbell Hausdorff expansion;
1 D	One dimension;
3 D	Three dimension;

Contents

Abstract

Analytic description of radio-frequency (RF) pulses involving quadrupolar spins (I >1/2) in NMR spectroscopy is fraught with difficulty due to large quadrupolar couplings. In this thesis, a modest attempt is made to present an analytic description of pulse experiments involving quadrupolar spins. Specifically, the spin dynamics during selective and non-selective excitation is described using effective RF Hamiltonians. The formalism presented provides a framework for deriving the optimum flip-angles required for selective and non-selective excitations and is in excellent agreement with numerical simulations.

Chapter 1

Introduction

Nuclear magnetic resonance (NMR) spectroscopy is one of the most commonly employed techniques for determining structure at molecular level [1]. Along with X-ray crystallography, it forms the basis for determining the molecular three-dimensional (3D) structure in a wide range of systems ranging from simple organic compounds to large bio-molecules. In contrast to the microwave (MW), Infrared (IR) and Ultraviolet (UV) spectroscopic techniques, NMR is less sensitive with poor signal to noise ratio. Nevertheless, the versatility in the form of flexibility that it provides with regard to the manipulation of interactions at atomic level makes it the most popular tool for structural characterization [2-6]. Subsequently, suites of techniques with differing complexities ranging from simple 1D to multi-dimensional experiments have emerged resulting in an overall improvement of our understanding of the causal relationship between structure and function [7, 8, 9]. With recent technological advancements and innovations in the form of high field magnets, probes etc., NMR has rightly become a viable alternative for structure determination both in the solution and solid state in both orderly and disorderly systems [10].

In addition to being employed as a structural tool, NMR spectroscopy provides a platform for understanding the foundations of modern physics (e.g. quantum mechanics, statistical mechanics etc.). Specifically, improvements in our understanding of the theoretical foundations of quantum mechanics [11] has extended the domain of NMR spectroscopy from typical chemistry labs to medicine (in the form of magnetic resonance imaging (MRI)), material science (in the form of Spintronics) and computer industry (in the form of memory devices, quantum computing) [7]. These interesting applications have resulted mainly due to our improved understanding of the nuclear spin interactions at the atomic level. Hence, improvement in our understanding of the nuclear spin interactions is quintessential to further extend the utility of NMR spectroscopy [12-20].

With this objective in mind, we make an attempt in understanding the dynamics of nuclear spins in the presence of non-commuting Hamiltonians [21-24]. Specifically, we attempt to derive an effective Hamiltonian that could be employed to describe pulse-NMR experiments involving quadrupolar spins. Although the dynamics of spin I = 1/2 systems is well understood and thoroughly described in the literature, theoretical descriptions involving quadrupolar spins (I > 1/2) are often fraught with difficulty due to larger magnitude of the quadrupolar interactions [25-26]. The problem gets further complicated with the non-commuting nature of the internal spin Hamiltonians. To address this issue, a modest attempt employing matrix mechanics is proposed in this thesis that could probably lead to a solution for this problem.

After a brief introduction to the basic concepts in this chapter, the concept of effective Hamiltonians in pulsed experiments is discussed in chapter-2. A detailed description of pulse experiments involving quadrupolar spins is presented in chapter-3, followed by a brief summary and possible extensions in future.

1.1 Basics of NMR

The phenomenon of NMR arises from the interaction between the nuclear spin magnetic moment with the applied external magnetic field [1]. To facilitate this process, an external magnetic field is applied to lift the degeneracy of the nuclear spin energy levels. The chapter begins with elementary aspects of NMR dealing with the concept of nuclear spin, magnetism and the nuclear spin interactions [8] that enable in the characterization of a sample. An elementary introduction to the spin dynamics is presented at the end of the chapter.

1.1.1 Nuclear spin and magnetism

The concept of nuclear spin is highly abstract and is introduced here only for explaining the known experimental results. In contrast to other spectroscopic techniques, NMR spectroscopy presents an attractive feature wherein the nuclear spin interactions could be manipulated at the atomic level. In addition to the classical orbital angular momentum, nuclei also possess an additional component to the angular momentum due to spin [8], also referred to as spin angular momentum and characterized by I, the spin quantum number. The resulting spin angular momentum induces a magnetic moment in the sample and facilitates the interaction between the sample and the electromagnetic radiation. Being an intrinsic property, the nuclear magnetic moment is related to the inherent spin angular momentum by the following relation,

$$\mu = \gamma \hbar I \tag{1.1}$$

where γ is the gyromagnetic ratio (rad/s), a constant characteristic of a particular nucleus. The interaction energy between the nuclear spin with the external magnetic field is represented by,

$$E = -\mu \bullet B_0 \tag{1.2}$$

wherein, B_0 represents the strength of the applied external magnetic field. If, the external magnetic field direction is chosen to be along the z-direction, the above equation reduces to,

$$E = -\gamma \hbar I_z B_0 \tag{1.3}$$

In the quantum mechanical framework, the observed interaction energy is re-expressed in terms of the nuclear spin Hamiltonian operator also referred to as the Zeeman Hamiltonian.

$$H_z = -\gamma \hbar I_z B_0 \tag{1.4}$$

with I_z denoting the spin angular momentum operator along the z –direction. Based on the above description, nuclei with $I = 0$ are unaffected by the external magnetic field or in other words are NMR inactive.

1.1.2 Spin angular momentum operators

In quantum mechanics every observable is associated with an operator. Consequently, the spin angular momentum exhibited by the nucleus is associated with four operators. The component of the spin angular momentum along the x, y, z directions is represented by the operators $\hat{I}_x$, $\hat{I}_y$, $\hat{I}_z$ respectively. The magnitude I ($I = \sqrt{I(I+1)}\hbar$) of the spin angular momentum vector is represented by the $\hat{I}^2$ operator (i.e. $\hat{I}^2 = \hat{I}_x{}^2 + \hat{I}_y{}^2 + \hat{I}_z{}^2$). To complete the description, the commutator relationship between the spin operators is represented by, $\left[\hat{I}_{\alpha},\hat{I}_{\beta}\right]=i\hbar\hat{I}_{\gamma}$ where α,β,γ are permuted cyclically among x,y,z . Additionally, all the three spin-operators commute with the $\hat{I}^2$ operator i.e. $\left[\hat{I}^2,\hat{I}_{\alpha}\right]=0$

1.1.3 Spin Eigen states

Each nucleus with spin quantum number 'I' is associated with 2I+1 spin states. In the presence of a large static magnetic field, the degeneracy between the spin states is lifted facilitating the observation of transitions between the spin levels. In general, the basis state of a system in quantum mechanics is constructed from the maximum set of commuting observables i.e. the observables associated with maximum set of commuting operators. Based on the commutator relations described in the previous section, only the square of the angular momentum operator along with one of the components of the angular momentum vector are measurable at a given instant of time. Hence, as a matter of convention, the spin states are constructed using the observables associated with $\hat{I}^2$ and $\hat{I}_z$ operators [1-8]. Employing the Dirac's bra-ket notation, the spin state for a single spin system is represented by the eigen-ket, $|I\,\mathrm{m}\rangle$. In the above representation, the coefficients *I, m* correspond to the eigenvalues associated with $\hat{I}^2$ and $\hat{I}_z$ operators respectively.

$$\hat{I}^2|I\,\mathrm{m}\rangle=I\left(I+1\right)|I\,\mathrm{m}\rangle \tag{1.5}$$

$$\hat{I}_z|I\,\mathrm{m}\rangle=m|I\,\mathrm{m}\rangle \tag{1.6}$$

To measure the components of the angular momentum along x and y direction, raising and lowering operators are defined.

$$\hat{I}^+=\hat{I}_x+i\hat{I}_y \tag{1.7}$$

$$\hat{I}^-=\hat{I}_x-i\hat{I}_y \tag{1.8}$$

The action of these operators on the spin state is described below,

$$\hat{I}^+|I\ \mathrm{m}\rangle=\sqrt{\{I(I+1)-m(m+1)\}}\,|I\ \mathrm{m+1}\rangle \quad \text{(1.9a)}$$

$$\hat{I}^-|I\ \mathrm{m}\rangle=\sqrt{\{I(I+1)-m(m-1)\}}\,|I\ \mathrm{m\text{-}1}\rangle \quad \text{1.9b)}$$

1.1.4 Matrix representation of spin operators

(a) Single spin system

In the matrix formulation, the spin states and operators are represented by matrices [8]. Depending on the magnitude of '*I*', the ket-states and bra-states are represented by column & row vectors of dimension $(2I+1)\times 1$ and $1\times(2I+1)$ respectively. The spin operators are represented by matrices of dimension $(2I+1)\times(2I+1)$.

For example, the spin operators for a spin-1/2 nucleus are represented by a 2×2 matrix,

$$I_Z = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \qquad I^+ = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}, \qquad I^- = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix},$$

$$I_Y = \frac{i}{2}\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} \qquad I_X = \frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad I^2 = \frac{3}{4}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

Similarly, spin operators for a spin-3/2 nucleus are represented by 4×4 matrix as following:

$$I_Z = \frac{1}{2}\begin{bmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{bmatrix}, \quad I^+ = \frac{1}{2}\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & 0 & 0 \end{bmatrix}, \quad I^- = \frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ \sqrt{3} & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix}$$

$$I^2 = \frac{15}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \quad I_Y = \frac{i}{2}\begin{bmatrix} 0 & -\sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & -2 & 0 \\ 0 & 2 & 0 & -\sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix} \quad I_X = \frac{1}{2}\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix}$$

(b) Two spin system

Employing the principle of spin angular momentum [11], the description of basis sets could be extended to coupled spin systems. Since, the vector addition of spin basis states corresponding to different spins are orthogonal, the basis set for a coupled spin system is constructed by a direct product of the individual basis set i.e. $|I_1 m_1 I_2 m_2\rangle = |I_1\ \mathrm{m}_1\rangle \otimes |I_2\ \mathrm{m}_2\rangle$.

For example, the spin operators for a system of two spin-1/2 nucleus are represented by a 4×4 matrix,

$$I_{1Z}=\frac{1}{2}\begin{bmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{bmatrix},\qquad I_1^+=\begin{bmatrix}0&0&1&0\\0&0&0&1\\0&0&0&0\\0&0&0&0\end{bmatrix},\qquad I_1^-=\begin{bmatrix}0&0&0&0\\0&0&0&0\\1&0&0&0\\0&1&0&0\end{bmatrix},$$

$$I_{2Z}=\frac{1}{2}\begin{bmatrix}1&0&0&0\\0&-1&0&0\\0&0&1&0\\0&0&0&-1\end{bmatrix}\qquad I_2^+=\begin{bmatrix}0&1&0&0\\0&0&0&0\\0&0&0&1\\0&0&0&0\end{bmatrix},\qquad I_2^-=\begin{bmatrix}0&0&0&0\\1&0&0&0\\0&0&0&0\\0&0&1&0\end{bmatrix},$$

$$I_{1X}=\frac{1}{2}\begin{bmatrix}0&0&1&0\\0&0&0&1\\1&0&0&0\\0&1&0&0\end{bmatrix},\qquad I_{1Y}=\frac{i}{2}\begin{bmatrix}0&0&-1&0\\0&0&0&-1\\1&0&0&0\\0&1&0&0\end{bmatrix},\qquad I_1^2=\frac{3}{4}\begin{bmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{bmatrix},$$

$$I_{2X}=\frac{1}{2}\begin{bmatrix}0&1&0&0\\1&0&0&0\\0&0&0&1\\0&0&1&0\end{bmatrix},\qquad I_{2Y}=\frac{i}{2}\begin{bmatrix}0&-1&0&0\\1&0&0&0\\0&0&0&-1\\0&0&1&0\end{bmatrix},\qquad I_2^2=\frac{3}{4}\begin{bmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{bmatrix},$$

where I_{1Z}, I_{1X}, I_{1Y}, I_1^+, I_1^-, I_1^2 are spin operators corresponding to nucleus-1, while I_2^-, I_2^+, I_{2Z}, I_{2X}, I_{2Y}, I_2^2 are spin operators corresponding to nucleus-2.

1.1.5 Density operator

Since measurements in NMR are made on collection of quantum mechanical systems, the concept of density matrix was introduced in quantum mechanics by Von Neumann in 1927. The density matrix in quantum mechanics is analogous to the distribution function in classical statistical mechanics [1, 8, and 27]. It provides a more general description to a collection of spin system, without referring to the individual spin states. Employing the bra-ket formulation, the density operator 'ρ' is represented by,

$$\rho=\sum_{ij}c_{ij}\left|\psi_i\right\rangle\left\langle\psi_j\right|, \tag{1.10}$$

where, 'c_{ij}'s represent probability amplitudes. $\left|\psi\right\rangle$ denotes the state function, and is expressed in terms of orthonormal basis states given by,

$$\left|\psi_i\right\rangle=\sum_{k=1}^{N}a_k^i\left|\phi_k\right\rangle. \tag{1.11}$$

The expectation value of an observable is calculated by evaluating the following equation,

$$\langle \hat{O}p \rangle = Tr[\rho.\hat{O}p] \tag{1.12}$$

To illustrate the utility of this formalism, let us consider a system comprising of identical spin-1/2 nuclei. The density operator for such a system is represented by, $\rho = |\psi\rangle\langle\psi|$. Here, $|\psi\rangle$ and $\langle\psi|$ are represented through column and row vectors given below.

$$|\psi\rangle = \begin{bmatrix} c_\alpha & c_\beta \end{bmatrix} \tag{1.13a}$$

$$\langle\psi| = \begin{bmatrix} c_\alpha^* \\ c_\beta^* \end{bmatrix} \tag{1.13b}$$

The coefficients c_α and c_β represents superposition constants and are normalized $\left(|c_\alpha|^2 + |c_\beta|^2 = 1\right)$.

Using eqns. (1.13a) and (1.13b), the density operator is expressed as:

$$\rho = \begin{bmatrix} c_\alpha^* \\ c_\beta^* \end{bmatrix} . \begin{bmatrix} c_\alpha & c_\beta \end{bmatrix} = \begin{bmatrix} c_\alpha c_\alpha^* & c_\alpha c_\beta^* \\ c_\beta c_\alpha^* & c_\beta c_\beta^* \end{bmatrix} \tag{1.14}$$

The diagonal elements of the spin density matrix $c_\alpha c_\alpha^*$ and $c_\beta c_\beta^*$ depict the population of the two states, while the off-diagonal terms $c_\alpha c_\beta^*$ and $c_\beta c_\alpha^*$ represent the coherences [8].

1.1.6 Density operator at thermal equilibrium

In the density matrix formalism, the density operator at thermal equilibrium acts as the initial state and forms the basis for subsequent description of spin dynamics [1].

Since, determination of exact initial density operator is difficult, statistics is often employed to approximate the populations and coherences at thermal equilibrium. A system that has been left unperturbed for long is expected to be in thermal equilibrium state. To beginwith, the populations are governed by the Boltzmann distribution and the coherences are assumed to be zero.

For example, consider a system consisting of spin-1/2 nuclei, with energy eigenstates $|\alpha\rangle$ and $|\beta\rangle$. Based on eqn. (1.3), the energy of the two states are given by:

$$E_\alpha = -\frac{1}{2}\gamma\hbar B_0 \quad (1.15a)$$

$$E_\beta = \frac{1}{2}\gamma\hbar B_0 \quad (1.15b)$$

Subsequently, based on Boltzmann distribution the population of α and β states is given by,

$$\mathrm{P}_\alpha = \frac{\exp\{-E_\alpha / k_B T\}}{\exp\{-E_\alpha / k_B T\} + \exp\{-E_\beta / k_B T\}}, \quad (1.16a)$$

$$\mathrm{P}_\beta = \frac{\exp\{-E_\beta / k_B T\}}{\exp\{-E_\alpha / k_B T\} + \exp\{-E_\beta / k_B T\}} \quad (1.16b)$$

where, E_α and E_β are energies of the two states described by eqn. (1.15a) and (1.15b), k_B is Boltzmann constant, T is absolute temperature at thermal equilibrium.

Since the energy difference between the two eigenstates is comparable to that of the available thermal energy ($k_B T$), population difference between the two states is very small at thermal equilibrium.

Consequently the exponential factors in eqn. (1.16) are approximated by,

$$\exp\{-E_\alpha / k_B T\} \cong 1 + \frac{\mathrm{B}}{2} \quad (1.17a)$$

$$\exp\{-E_\beta / k_B T\} \cong 1 - \frac{\mathrm{B}}{2} \quad (1.17b)$$

where, $\mathrm{B} = \frac{\hbar\gamma B_0}{k_B T}$.

Employing eqns. (1.17a) and (1.17b), the population of the two states is represented as:

$$\mathrm{P}_\alpha \cong \frac{1}{2} + \frac{\mathrm{B}}{4} \quad (1.18a)$$

$$\mathrm{P}_\beta \cong \frac{1}{2} - \frac{\mathrm{B}}{4} \quad (1.18b)$$

Thus, the density matrix at thermal equilibrium is represented by,

$$\rho = \begin{bmatrix} \frac{1}{2}+\frac{B}{4} & 0 \\ 0 & \frac{1}{2}-\frac{B}{4} \end{bmatrix}, \tag{1.19}$$

Employing the operators, the density operator is re-expressed as:

$$\rho = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \frac{B}{4}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \tag{1.20}$$

wherein, the first matrix is the identity operator and the second matrix is proportional to the I_Z operator, i.e.

$$\rho = \frac{1}{2}\hat{1} + \frac{B}{2} I_Z \tag{1.21}$$

1.2 Nuclear spin interactions in NMR

As described earlier, the external static magnetic field lifts the degeneracy of the $2I+1$ nuclear spin states. In the presence of an oscillating magnetic field, transition between the nuclear spin states are induced when the frequency of the oscillating magnetic field matches the energy separation between the spin states.

To quantify the experimental results, it is important to understand the spin interactions. To beginwith, the spin interactions are generally classified into external and internal interactions. The external interactions comprise of the Zeeman & RF interaction, while the internal interactions mainly comprise of (1) chemical shift (2) spin-spin coupling (3) dipolar coupling (4) quadrupolar interaction. Quantum mechanically the spin interactions are represented by means of Hamiltonian operators.

$$H = \underbrace{H_Z + H_{RF}}_{\text{external interactions}} + \underbrace{H_{CS} + H_J + H_D + H_Q}_{\text{internal interactions}} \tag{1.22}$$

where, H_Z (Zeeman interaction), H_{RF} (Radio Frequency interaction), H_{CS} (chemical shift interaction), H_J (spin-spin coupling), H_D (dipolar interactions), are magnetic in nature. While, H_Q (quadrupolar interaction) is electrical in nature, exhibited only by nuclei having non-spherical charge distribution (I >1/2).

1.2.1 Zeeman Interaction

The interaction between the magnetic moment of nuclei (with spin I) and external magnetic field is known as the Zeeman interaction. It is by far the largest interaction in NMR spectroscopy and is employed to lift the degeneracy of the spin states. This results in enhancing the net magnetization and results in the NMR signal.

Quantum mechanically, this interaction is represented by following Hamiltonian:

$$H_Z = -\sum_i \mu_{iZ} B_0 = -\hbar \sum_i \omega_{i0} I_{iZ} \qquad (1.23)$$

where, ω_{i0} is Larmor frequency of i[th] nucleus ($\omega_{i0} = \gamma_i B_0$), $\hbar$ is Planck's constant divided by 2π. γ_i gyromagnetic ratio of i[th] nucleus and B_0 is applied external magnetic field.

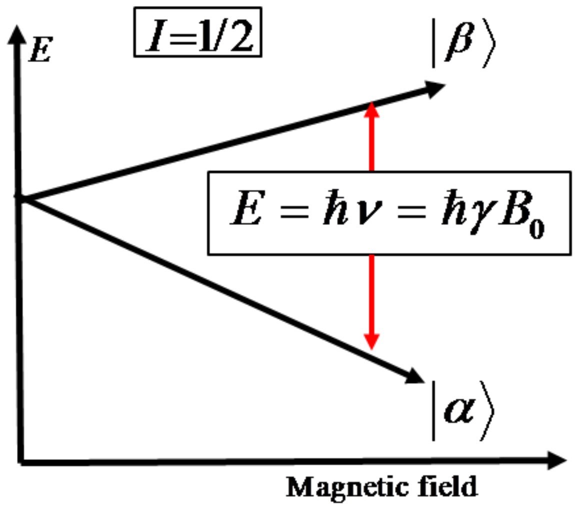

FIGURE 1. ZEEMAN SPLITTING IN SPIN I = 1/2 NUCLEUS.

In presence of external magnetic field degeneracy between two eigenstates $\left|\frac{1}{2},\frac{1}{2}\right\rangle$ and $\left|\frac{1}{2},-\frac{1}{2}\right\rangle$ get lifted.

Energy gap between two states is directly proportional to the strength of the applied external magnetic field.

1.2.2 Radio frequency interaction

In order to detect the NMR signal, an oscillating magnetic field is applied. The static external magnetic field lifts the degeneracy of the spin states, while the oscillating magnetic field induces transitions between the spin states when the frequency matches with the energy separation. The oscillating magnetic field applied along the x-axis is represented by,

$$B_{rf}(t) = -2B_1 \cos(\omega_{rf} t \pm \phi)\hat{i} \qquad (1.24)$$

Where, B_1 is amplitude, ω_{rf} is the frequency, ϕ the phase of the applied RF. $\hat{i}$ represents the unit vector along x-axis.

Quantum mechanically, this interaction is represented by the following Hamiltonian:

$$H_{RF} = -\mu \bullet B$$

$$H_{RF} = -2\hbar \sum_i \omega_{i1} I_{iX} \cos(\omega_{rf} t + \phi) \quad (1.25)$$

where, $\omega_{i1} = \gamma_i B$ is the amplitude of the applied oscillating magnetic field.

1.2.3 Chemical shift interaction

It refers to the interaction between the nuclear magnetic moment with the external magnetic field, mediated by the surrounding electron clouds. Since the electrons possess magnetic moment, the effective field experienced by the nucleus varies and is utilized in the characterization of nuclei of same kind in different chemical environments. For example, the methyl protons and methylene protons in ethanol experience different static magnetic fields due to differing electrical environments. Consequently, two peaks are observed in the ^{1}H-NMR spectrum. Depending on the relative orientation of the tiny induced magnetic field produced by the surrounding electrons, the net magnetic field experienced by the nucleus varies and is represented by,

$$B_i^{actual} = B_0 + B_i^{induced} \quad (1.26)$$

where, the induced magnetic field is denoted by $B_i^{induced} = \tilde{\sigma} B_0$. Being a second rank tensor '$\tilde{\sigma}$' is represented by,

$$\tilde{\sigma} = \begin{pmatrix} \sigma_{XX} & \sigma_{XY} & \sigma_{XZ} \\ \sigma_{YX} & \sigma_{YY} & \sigma_{YZ} \\ \sigma_{ZX} & \sigma_{ZY} & \sigma_{ZZ} \end{pmatrix} \quad (1.27)$$

In solid state NMR spectroscopy, broad chemical shift powder pattern (wide distribution of chemical shift) is observed due to lack of molecular motions. This dependence of chemical shift on orientation of crystal with respect to external magnetic field is defined as chemical shift anisotropy.

Quantum mechanically, the chemical shift interaction is described by,

$$H_{CS} = -\hbar \sum_i \gamma_i \vec{I}_i \tilde{\sigma} \vec{B}_0 \quad (1.28)$$

1.2.4 Spin-spin coupling interaction

The interactions between two nuclei mediated through bonding electrons are known as scalar or indirect or J-coupling. This is quite small in magnitude and is observed in both solution and solid state NMR spectroscopy. Quantum mechanically, it is represented by,

$$H_J = -\frac{1}{2}\sum_{i,k}\vec{I}_i.\tilde{J}.\vec{I}_k \tag{1.29}$$

wherein, $\tilde{J}$ is a second rank tensor analogous to the chemical shift tensor described in eqn. (1.27).

1.2.5 Dipolar interaction

The mutual interaction between two nuclei through space is referred to as dipolar interaction. The non zero magnetic moment, result in small magnetic fields around a nucleus, and enables in the interaction with the other nucleus. Due to rapid molecular motion, the dipolar interaction gets averaged in the solution state. However, the restricted mobility in the solid state results in non-zero value. The dipolar interaction is represented by,

$$H_D = \frac{\mu_0\hbar}{4\pi}\sum_{i<j}\frac{\gamma_i\gamma_j}{\left|\vec{r}_{ij}\right|^3}\vec{I}_i.\tilde{D}.\vec{I}_j \tag{1.30}$$

where, $\left|\vec{r}_{ij}\right|^3$ is the inter-nuclear distance vector, $\tilde{D}$ is second rank tensor called as dipolar coupling tensor.

Depending on the spins involved, the dipolar interactions are further classified into homonuclear (e.g. ^{1}H- ^{1}H) and heteronuclear (e.g. ^{13}C - ^{1}H).

The homonuclear dipolar interaction between spins I_1 and I_2 is represented by,

$$H_D = \frac{\mu_0\gamma^2\hbar}{8\pi\left|\vec{r}_{12}\right|^3}(1-3\cos^2\theta)\left[3I_{1Z}I_{2Z} - I_1.I_2\right] \tag{1.31}$$

while, heteronuclear dipolar interaction between spins I and S can be described by,

$$H_D = \frac{\mu_0\gamma_I\gamma_S\hbar}{4\pi\left|\vec{r}_{IS}\right|^3}(1-3\cos^2\theta)\left[I_Z S_Z\right] \tag{1.32}$$

1.2.6 Quadrupolar interaction

The quadrupolar interaction is defined as the interaction between nuclear quadrupolar moment with the electric field gradient. In nuclei with I >1/2, quadrupolar moment results due to non-spherical distribution of charge. Additionally, the unsymmetrical electric charge distribution in such systems produces an electric field gradient. Quantum mechanically, this interaction is represented by,

$$H_Q = \hat{I}.\tilde{Q}.\hat{I} \tag{1.33}$$

where, $\tilde{Q} = \frac{eQ}{2I(2I-1)h}\tilde{V}$ is quadrupolar coupling tensor. Q is quadrupolar constant, eQ gives nuclear quadrupolar moment, $\tilde{V}$ is second rank electric field gradient (EFG) tensor.

Depending on, the magnitude of the various terms the quadrupolar Hamiltonian, [eqn. (1.33)] is rewritten by,

$$H_Q = H_Q^{(1)} + H_Q^{(2)} + ... \tag{1.34}$$

where, $H_Q^{(1)}$ is first order quadrupolar Hamiltonian, given by:

$$H_Q^{(1)} = \frac{\omega_Q}{6}\{3I_Z^2 - I^2\} \tag{1.35}$$

$H_Q^{(2)}$ is second order qudrupolar Hamiltonian, given by:

$$H_Q^{(2)} = \frac{\omega_Q}{6}.\frac{\eta_Q}{2}\{I_+^2 + I_-^2\} \tag{1.36}$$

with the $\omega_Q = \frac{3e^2qQ}{2I(2I-1)\hbar}$ (rad/s).

Chapter 2

This chapter describes the effect of pulses in NMR for spin-1/2 system using effective RF Hamiltonian approach. As a test case we demonstrate the utility of this approach for describing the cross-polarization experiment involving spin I = 1/2 nuclei.

2.1 Description of pulses in NMR: An Effective RF Hamiltonian approach

To beginwith, let us consider the description of a single spin (I=1/2) system in the presence of both static and an oscillating magnetic field. The Hamiltonian for such a system is represented by,

$$H = -\hbar\omega_0 I_z - 2\hbar\omega_1 \cos(\omega_{rf} t).I_x \qquad (2.1)$$

where 'ω_0' is the Larmor frequency ($\omega_0 = \gamma B_0$) and 'ω_1' the amplitude ($\omega_1 = \gamma B_1$) of the RF field ('ω_{rf}' denotes the frequency of the oscillating magnetic field and is often comparable to that of ω_0). For the sake of illustration, the oscillating field is chosen along the x-direction.

The time evolution of a quantum system is described by the quantum-Liouville equation[1, 29],

$$i\hbar \frac{d\rho(t)}{dt} = \left[H, \rho(t)\right] \qquad (2.2)$$

where, '$\rho(t)$' is defined as the density operator and is analogous to the wave function in the traditional Schrödinger equation. The formal solution to the above Liouville equation (eqn.2.2) incorporating the explicit time-dependence of the Hamiltonian is represented by [1, 29],

$$\rho(t) = \hat{T}\exp\left\{-\frac{i}{\hbar}\int_0^t H(t')dt'\right\}\ \rho(0)\ \hat{T}\exp\left\{\frac{i}{\hbar}\int_0^t H(t')dt'\right\} \qquad (2.3)$$

In cases where the Hamiltonian is time-independent, the solution reduces to a much simpler form as illustrated below,

$$\rho(t) = \exp\left\{-\frac{i}{\hbar}Ht\right\}\rho(0)\exp\left\{\frac{i}{\hbar}Ht\right\} \tag{2.4}$$

To reduce the complexity in the description of the density operator, effective Hamiltonians have been proposed in the past for facilitating analytic description of the quantum dynamics [7]. Here, we present an analytic description of the spin dynamics during RF pulses in NMR experiments. For the sake of simplicity, we confine our discussion to a single-pulse experiment.

Case-A

In the first approach, the spin system is transformed into the Zeeman interaction frame defined by,

$$\tilde{\rho}(t) = \exp\left\{\frac{i}{\hbar}H_0 t\right\}\rho(t)\exp\left\{-\frac{i}{\hbar}H_0 t\right\} \tag{2.5}$$

where $H_0 = -\hbar\omega_0 I_z$ and $H_1(t) = -2\hbar\omega_1 \cos(\omega_{rf} t)\, I_x$.

Subsequently, the Liouville equation in this new frame is represented by,

$$i\hbar\frac{d\tilde{\rho}(t)}{dt} = \left[H, \tilde{\rho}(t)\right] \tag{2.6}$$

Since, the magnitude of H_0 is much larger in comparison to that of H_1, the unitary transformation (see eqn. 2.6) basically gets rid of H_0 in the new frame. However, the RF Hamiltonian H_1 is still time-dependent in this new frame and gains additional time-dependence due to H_0 as represented below,

$$\begin{aligned}\tilde{H}_1(t) &= \exp\left\{\frac{i}{\hbar}H_0 t\right\}H_1(t)\exp\left\{-\frac{i}{\hbar}H_0 t\right\} \\ &= -\hbar\omega_1\left[I_x \cos\left(\omega_{rf} - \omega_0\right)t + I_x \cos\left(\omega_{rf} + \omega_0\right)t\right] + \\ &\quad -\hbar\omega_1\left[I_y \sin\left(\omega_{rf} - \omega_0\right)t + I_y \sin\left(\omega_{rf} + \omega_0\right)t\right]\end{aligned} \tag{2.7}$$

At the exact resonance condition (i.e. $\omega_{rf} = \omega_0$), the above Hamiltonian (eqn. 2.7) is further simplified by neglecting the high frequency terms ($\propto 2\omega_0$) under secular approximation,

$$\tilde{H}_1 = -\hbar\omega_1\, I_x \tag{2.8}$$

Employing this approximation [1, 20], the evolution of the system in the interaction frame is described by,

$$\tilde{\rho}(t) = \exp\left\{\frac{i}{\hbar}H_1 t\right\}\tilde{\rho}(0)\exp\left\{-\frac{i}{\hbar}H_1 t\right\} \tag{2.9}$$

with $\tilde{\rho}(0) = \rho(0)$ being the initial condition in the interaction frame.

Since, the amplitude (ω_1) of the pulse is much larger in comparison to the internal spin interactions (such as chemical shift, dipolar and J-coupling), the time evolution of the system is mainly governed by the RF Hamiltonian 'H_1' during a pulse.

In the interaction frame, the density operator at the end of single pulse of duration t_p, is represented by,

$$\tilde{\rho}(t_p) = \exp(i\omega_1 t_p I_x)\tilde{\rho}(0)\exp(-i\omega_1 t_p I_x) \qquad (2.10)$$

For a typical $\left(\frac{\pi}{2}\right)_x$ pulse (i.e. $\omega_1 t_P = \frac{\pi}{2}$), the initial magnetization along z-direction is flipped to the y-direction i.e. $\tilde{\rho}(t_p) = I_y$. Subsequently, after, the pulse is switched off, the system does not evolve in the interaction frame i.e. $\tilde{\rho}(t_p + \tau) = \tilde{\rho}(t_p) = I_y$ (where 'τ' is the duration after the pulse).

The expectation value of an observable is calculated using Eq. (2.11),

$$\begin{aligned}\left\langle I_y(\tau)\right\rangle &= \text{Trace}\left[I_y.\,\rho(\tau)\right] = \text{Trace}\left[I_y.\ \exp\left\{-\frac{i}{\hbar}H_0\tau\right\}\tilde{\rho}(\tau)\exp\left\{\frac{i}{\hbar}H_0\tau\right\}\right] \\ &= \text{Trace}\left[\underbrace{\exp\left\{\frac{i}{\hbar}H_0\tau\right\}I_y\exp\left\{-\frac{i}{\hbar}H_0\tau\right\}}_{\tilde{I}_y}\ .\ \tilde{\rho}(\tau)\right] = \text{Trace}\left[\tilde{I}_y(\tau).\ \tilde{\rho}(\tau)\right]\end{aligned} \qquad (2.11)$$

From Eq. (2.11) it is clear that the expectation value of an observable is independent of the frame of reference. In contrast to the description in the lab frame, both the density operator and the detection operator are time-dependent in the interaction picture. On further evaluation, the final result leads to,

$$\left\langle I_y(\tau)\right\rangle = \cos\omega_0\tau.\text{Trace}\left[I_y^2\right] \qquad (2.12)$$

In the absence of dissipative processes, the magnetization [NMR signal, see eqn. (2.12)] is oscillatory, and the Fourier transform of the time-domain signal [eqn. (2.12)], yields the frequency spectrum (stick spectrum). However, in a real system, the spins interact among themselves in addition to the interaction with the surrounding lattice. Consequently, the time-domain signal decays with time (commonly referred to as Free-induction decay (FID)). To mimic the experimental spectrum, the above time-domain signal is often multiplied by a phenomenological damping term (denoted by T_2, commonly referred to as the spin-spin relaxation time). Experimentally, the spin-spin relaxation constant is roughly estimated from the line-width of the peaks [1] observed in the spectrum.

$$\left\langle I_y(\tau)\right\rangle = \cos\omega_0\tau.\exp\left(-\frac{\tau}{T_2}\right) \tag{2.13}$$

Case-B

In the second approach, the system is transformed into the interaction frame defined by the RF-pulse, i.e. $\tilde{\rho}(t) = \exp(-i\omega_{rf}t)\rho(t)\exp(i\omega_{rf}t)$ where 'ω_{rf}' is the frequency of the oscillating magnetic field. Employing the standard algebra in NMR (including the secular approximation), the equation of motion in the Liouville space is represented by,

$$i\hbar\frac{d\tilde{\rho}(t)}{dt} = \left[-\hbar\Delta\omega I_z - \hbar\omega_1 I_x, \tilde{\rho}(t)\right] \tag{2.14}$$

where, $\Delta\omega = \left(\omega_{rf} - \omega_0\right)$ is the off-set. Since the two operators (I_x, I_z) are non-commuting, a closed form solution to the above equation (eqn. 2.14) is bit complicated. To circumvent this problem, the standard approach involves the neglect of the off-set term during the pulse. Such an approach holds well as long as the off-set is smaller in magnitude in comparison to the RF amplitude i.e. $\Delta\omega < \omega_1$. Hence, during the pulse, the spin system evolves only during the RF Hamiltonian ($\tilde{H}_1 = -\hbar\omega_1 I_x$),

$$\begin{aligned}\tilde{\rho}(t_p) &= \exp(i\omega_1 t_p I_x)\tilde{\rho}(0)\exp(-i\omega_1 t_p I_x)\\ &= I_y (\text{if } \omega_1 t_p = \tfrac{\pi}{2})\end{aligned} \tag{2.15}$$

In contrast to the earlier approach, the system evolves under the off-set term, after the pulse is switched off i.e.

$$\begin{aligned}\tilde{\rho}(t_p+\tau) &= \exp(i\Delta\omega\tau I_z)\tilde{\rho}(t_p)\exp(-i\Delta\omega\tau I_z)\\ &= I_y\cos\Delta\omega\tau + I_x\cos\Delta\omega\tau\end{aligned} \tag{2.16}$$

Following the standard procedure, the expectation value is calculated and represented below,

$$\begin{aligned}\left\langle I_y(\tau)\right\rangle &= \text{Trace}\left[\tilde{I}_y(\tau).\ \tilde{\rho}(\tau)\right]\\ &= \text{Trace}\left[\left(I_y\cos\omega_{rf}\tau + I_x\sin\omega_{rf}\tau\right).\left(I_y\cos\Delta\omega\tau + I_x\sin\Delta\omega\tau\right)\right]\\ &= \tfrac{1}{2}\cos\omega_0\tau.\text{Trace}\left[I_y^2\right] + \tfrac{1}{2}\cos\omega_0\tau.\text{Trace}\left[I_x^2\right]\\ &= \cos\omega_0\tau\end{aligned} \tag{2.17}$$

Not surprisingly, the final result is similar to the one derived in the previous section. Hence, the derived effective RF Hamiltonians and the approximations employed seem to provide some physical insights into our understanding of pulse-NMR experiments.

2.2 Cross-Polarization experiment for spin-1/2 system

To improve the sensitivity of NMR experiments involving low abundant/less sensitive nuclei, nuclear double resonance experiment [2] in the form of cross-polarization (CP) experiments were developed in NMR. In the CP experiment, the sensitivity of low abundant nuclei is improved when a thermal contact is established between the low gamma nucleus with high gamma nucleus [6]. Experimentally, this is implemented when the precessional rates of the two types of nuclei is matched facilitating the transfer of polarization through the dipolar interactions. In Figure 2, the basic CP scheme is depicted wherein the polarization transfer from sensitive ^{1}H nuclei (I =1/2) is transferred to the less sensitive (insensitive) ^{13}C nuclei (I =1/2).

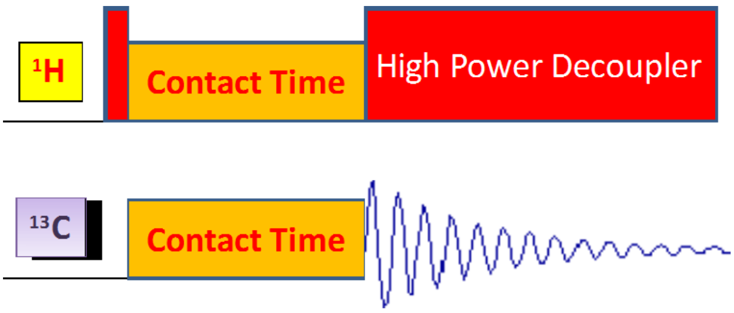

FIGURE 2 PULSE SEQUENCE FOR CP EXPERIMENT

A qualitative picture employing simple vector model is depicted in Figure 3. Initially both the nuclei are at thermal equilibrium. The experiment begins with a 90^0 pulse along Y-direction on the proton channel. The resulting polarization along the X-axis is locked by a constant magnetic field (commonly referred to as spin-locking field) of strength B_{1H} applied along X-direction. To facilitate polarization transfer between the spins, an additional RF field of strength B_{1C} is applied on the carbon channel. To maximize the polarization transfer, the RF fields employed on the two channels are adjusted such that they satisfy the Hartmann-Hahn condition ($\gamma_H B_{1H} = \gamma_C B_{1C}$) [2].

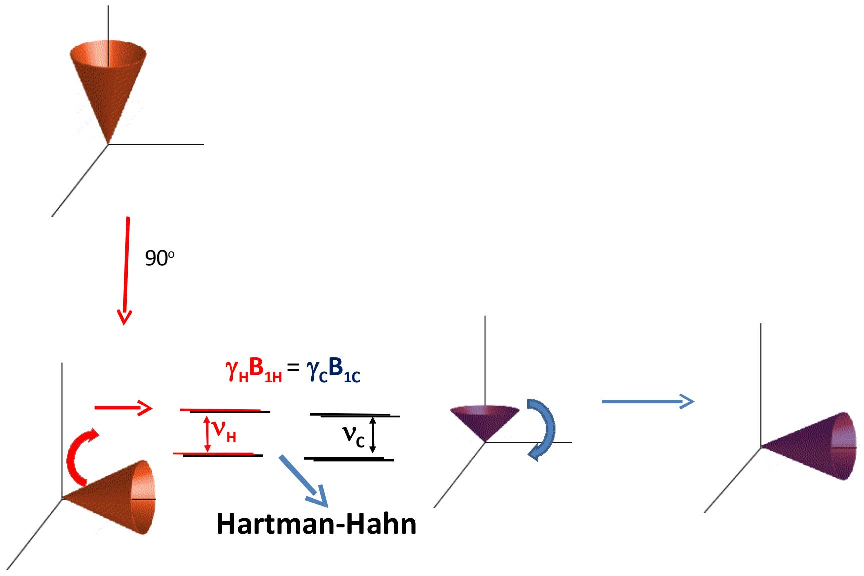

FIGURE 3 PICTORIAL DEPICTION OF CP EXPERIMENT

In figure brown color vector denotes ^{1}H polarization, while violet color vector denotes ^{13}C polarization.

To give a formal description of this process, the cross-polarization experiment involving two spin-1/2 nuclei, is described using the effective RF Hamiltonian formalism.

2.2.1 Hamiltonian

To elucidate the mechanism of polarization transfer among spins, we employ a model two spin system. The spin Hamiltonian for an isolated two spin system is represented by,

$$H = H_I + H_S + H_{IS} \tag{2.18}$$

where, H_I and H_S are single spin Hamiltonians, while H_{IS} is the two spin Hamiltonian. The Hamiltonian for spins 'I' and 'S' is represented below,

$$H_I = -\hbar\omega_{0I} I_z - 2\hbar\omega_{1I} \cos(\omega_{rf,I} t).I_x \tag{2.19a}$$

$$H_S = -\hbar\omega_{0S} S_z - 2\hbar\omega_{1S} \cos(\omega_{rf,S} t).S_x \tag{2.19b}$$

In the above expressions $\omega_{1I} = \gamma_I B_{1I}$ is the amplitude of the RF field on channel *I*, γ_I is gyromagnetic ratio of spin *I* and B_{1I} is amplitude of the RF on channel *I*. ω_{0I} is Larmor frequency and $\omega_{rf,I}$ is spectrometer operating frequency of spin-*I* nucleus.

The dipolar Hamiltonian is described by,

$$H_{IS} = dI_z S_z, \tag{2.20}$$

where, $d = \frac{\gamma_I \gamma_S \hbar}{r_{IS}^3}(1 - 3\cos^2\theta)$ is the dipolar constant.

(A) Rotating frame transformation

To study the effect of the RF field on the internal interactions, the spin Hamiltonian is transformed into the rotating interaction frame via the unitary transformation defined below,

$$U_1 = \exp(-i\omega_{rf,I} t I_z).\exp(-i\omega_{rf,S} t S_z) \tag{2.21}$$

The objective of such a transformation is to remove the contributions arising from the Zeeman interaction.

In the rotating frame, the single spin Hamiltonian is transformed as depicted below, $H_I^{rot} = U_1 H_I U_1^{-1}$

$$H_I^{rot} = -\hbar(\omega_{0I} - \omega_{rf,I}) I_Z - 2\hbar\omega_{1I}\cos(\omega_{rf,I} t)[I_X \cos(\omega_{rf,I} t) - I_Y \sin(\omega_{rf,I} t)] \tag{2.22a}$$

which on simplification results in

$$H_I^{rot} = -\hbar\Delta\omega_I I_Z - \hbar\omega_{1I}[I_X\{1 + \cos 2(\omega_{rf,I} t) - I_Y \sin 2(\omega_{rf,I} t)], \tag{2.22b}$$

where, $\Delta\omega_I$ is the chemical shift offset of spin I .

Employing the secular approximation, the high frequency terms in the above Hamiltonian are neglected and it reduces to a much simpler form given below,

$$H_I^{rot} = -\hbar\Delta\omega_I I_Z - \hbar\omega_{1I} I_X \tag{2.22c}$$

When the RF irradiation is on-resonance (i.e. $\Delta\omega = 0$), the Hamiltonian for the single spin in their respective rotating frames reduces to,

$$H_I^{rot} = -\hbar\omega_{1I} I_x . \tag{2.22}$$

$$H_S^{rot} = -\hbar\omega_{1S} S_x \tag{2.23}$$

Due to commuting nature the two spin Hamiltonian, it remains invariant in the rotating frame.

$$H_{IS}^{rot} = dI_z S_z \tag{2.24}$$

The overall Hamiltonian in the rotating frame is represented by,

$$H^{rot} = -\hbar\omega_{1I} I_x - \hbar\omega_{1S} S_x + dI_z S_z \tag{2.25}$$

Employing the product basis ($|m_I m_S\rangle$) the single spin Hamiltonian, and two spin Hamiltonian in the rotating frame are represented by,

$$H_I^{rot} = -\frac{\omega_{1I}}{2}\begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}, \quad H_S^{rot} = -\frac{\omega_{1S}}{2}\begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}, \quad H_{IS}^{rot} = \frac{d}{4}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

Since the dominant contributions (ω_{1I} and ω_{1s}) in the overall Hamiltonian (see below) are off-diagonal, an additional transformation is necessary for analytic description.

$$H^{rot} = -\begin{bmatrix} -\frac{d}{4} & \frac{\omega_{1S}}{2} & \frac{\omega_{1I}}{2} & 0 \\ \frac{\omega_{1S}}{2} & \frac{d}{4} & 0 & \frac{\omega_{1I}}{2} \\ \frac{\omega_{1I}}{2} & 0 & \frac{d}{4} & \frac{\omega_{1S}}{2} \\ 0 & \frac{\omega_{1I}}{2} & \frac{\omega_{1S}}{2} & -\frac{d}{4} \end{bmatrix}$$

(B) Tilted frame transformation

To fold the dominant contributions, the employed additional unitary transformation is defined below,

$$U_2 = \exp\left\{-i\frac{\pi}{2} I_y\right\}.\exp\left\{-i\frac{\pi}{2} S_y\right\} \tag{2.26}$$

In the tilted rotating frame the single spin Hamiltonian reduces to eqn. (2.27) & (2.28), while the two spin Hamiltonian reduces to eqn. (2.29).

$$H_I^{til} = -\hbar\omega_{1I} I_z \tag{2.27}$$

$$H_S^{til} = -\hbar\omega_{1S}S_z \tag{2.28}$$

$$H_{IS}^{til} = dI_xS_x \tag{2.29}$$

The overall Hamiltonian in the tilted rotating frame is represented by,

$$H^{til} = H_I^{til} + H_S^{til} + H_{IS}^{til}$$

$$H^{til} = -\hbar\omega_{1I}I_z - \hbar\omega_{1S}S_z + dI_xS_x \tag{2.30}$$

In the tilted rotating frame the overall Hamiltonian is nearly diagonal (see below)

$$H^{til} = \begin{bmatrix} -\frac{1}{2}(\omega_{1I}+\omega_{1S}) & 0 & 0 & \frac{d}{4} \\ 0 & -\frac{1}{2}(\omega_{1I}-\omega_{1S}) & \frac{d}{4} & 0 \\ 0 & \frac{d}{4} & \frac{1}{2}(\omega_{1I}-\omega_{1S}) & 0 \\ \frac{d}{4} & 0 & 0 & \frac{1}{2}(\omega_{1I}+\omega_{1S}) \end{bmatrix}$$

(C) Hartmann-Hahn condition

To further simplify the description, a third unitary transformation defined by,

$$U_3 = \exp(-i\omega_{1I}tI_z).\exp(-i\omega_{1S}tS_z) \tag{2.31}$$

is performed.

$$H_{IS}^{dom} = U_3H_{IS}^{til}U_3^{-1}$$

$$\begin{aligned} H_{IS}^{dom} = &\underbrace{\frac{d}{4}[I_+S_+\exp\{-i(\omega_{1I}+\omega_{1S})t\} + I_-S_-\exp\{i(\omega_{1I}+\omega_{1S})t\}]}_{DQ} \\ &+\underbrace{\frac{d}{4}[I_+S_-\exp\{-i(\omega_{1I}-\omega_{1S})t\} + I_-S_+\{i(\omega_{1I}-\omega_{1S})t\}]}_{ZQ} \end{aligned} \tag{2.32}$$

The resulting two spin Hamiltonian comprises of double quantum (DQ) and zero quantum (ZQ) operators.

When the RF amplitudes on two channels are matched, $\omega_{1I} = \omega_{1S}$, a time independent

Hamiltonian, (formally known as Hartmann-Hahn matching condition) is obtained.

$$H_{eff} = \frac{d}{4}[I^+S^- + I^-S^+] \quad (2.33)$$

The high frequency terms associated with DQ operators are neglected under secular approximation.

2.2.2 Detection operator

Theoretically, the time domain NMR signal is evaluated by calculating the expectation value of the S_x operator.

$$\langle S_x \rangle = Tr[\rho(t).S_x] = Tr[\rho_{eff}(t).S_{x,eff}] \quad (2.34)$$

To have a consistent description, the detection operator is transformed by the transformations described in the previous section.

$$S_{x,eff} = -S_z \cos(\omega_{rf,S}t) + \sin(\omega_{rf,S}t)[S_y \cos(\omega_{1S}t) - S_x \sin(\omega_{1S}t)] \quad (2.35)$$

2.2.3 Density operator

At thermal equilibrium, the net magnetization for, both *I* and *S* lie along z-axis. In the high temperature approximation, the density operator ‘ ρ ’ is represented by,

$$\rho = \frac{1}{2}\hat{1} + \frac{\mathrm{B}}{2} I_z, \quad (2.36)$$

Since the identity operator is invariant the initial density matrix is often expressed by,

$$\rho(0) = \frac{\mathrm{B}}{2} I_z \quad (2.37)$$

(A) Pulse sequence

As shown in figure 2, pulse sequence of CP experiment consists of 90^0 pulse on *I* channel along y-direction. This results in rotation of density matrix along x-direction. The impact of this pulse on initial density matrix is described below,

$$\tilde{\rho}(0) = e^{i(\pi/2).I_y} \rho(0) e^{-i(\pi/2).I_y} \quad (2.38)$$

$$\Rightarrow \tilde{\rho}(0) = \frac{\mathrm{B}}{2} I_x \quad (2.39)$$

(B) Unitary transformations

Analogous to the detection operator, the initial density operator is transformed and represented by,

$$\rho_{eff}(0) = \frac{\mathrm{B}}{2}\left[-I_Z \cos(\omega_{rf,I}t) + \sin(\omega_{rf,I}t)[I_Y \cos(\omega_{1I}t) - I_X \sin(\omega_{1I}t)]\right] \tag{2.40}$$

(C) Evolution of density matrix

The time evolution of density operator is expressed by,

$$i\hbar \frac{d\rho(t)}{dt} = \left[H, \rho(t)\right] \tag{2.41}$$

Employing the BCH (Baker-Campbell-Hausdorff) expansion the formal solution is expressed by,

$$\rho(t) = \exp\left\{\frac{i}{\hbar}Ht\right\}\rho(0)\exp\left\{-\frac{i}{\hbar}Ht\right\} = \rho(0) + \left(\frac{i}{\hbar}t\right)\left[H, \rho(0)\right] + \frac{1}{2!}\left(\frac{i}{\hbar}t\right)^2\left[H,\left[H, \rho(0)\right]\right] + .. \tag{2.42}$$

which on further simplification reduces to,

$$\rho_{eff}(t) = \rho_{eff}(0) + \frac{d}{4}\left[\{I^+S^- + I^-S^+\}, \rho_{eff}(0)\right] + ... \tag{2.43}$$

$$S_{X,eff} = -S_Z \cos(\omega_{rf,S}t) + \sin(\omega_{rf,S}t)[S_Y \cos(\omega_{1S}t) - S_X \sin(\omega_{1S}t)]$$

$$\left\langle S_X \right\rangle = Tr[\rho_{eff}(t).S_{X,eff}]$$

The time domain signal is expressed by,

$$\begin{aligned}\left\langle S^+ \right\rangle = &-\frac{i}{4\hbar}d\sin(\omega_{rf,S}t)\cos(\omega_{1S}t).Tr\left[(I^+S^- - I^-S^+)S_y\right] \\ &-\frac{i}{4\hbar}d\sin(\omega_{rf,S}t)\sin(\omega_{1S}t).Tr\left[(-S^+I_Z + I_ZS^-)S_x\right]\end{aligned} \tag{2.44}$$

$$\begin{aligned}\left\langle S^+ \right\rangle &\propto d \\ &\propto \gamma_S\gamma_I\end{aligned} \tag{2.45}$$

In a typical experiment, the Signal $\left\langle S^+ \right\rangle$ is proportional to γ and in the case of CP it is proportional to γ_I (the abundant nuclei). Hence the signal of the *S* spin is enhanced due to CP. In case of polarization transfer from proton to carbon, the signal enhances up to 4 times ($\gamma_I = 4\gamma_S$).

2.2.4 Numerical simulations

To check the validity of the analytical theory described in the previous sections, simulations involving numerical integration of Liouville equation were performed and compared with the analytical simulations.

In the simulations presented, polarization transfer from ^{1}H to ^{13}C is evaluated as the function of mixing time. The analytical results agree well with the numerical simulations and confirm the validity of the approach presented.

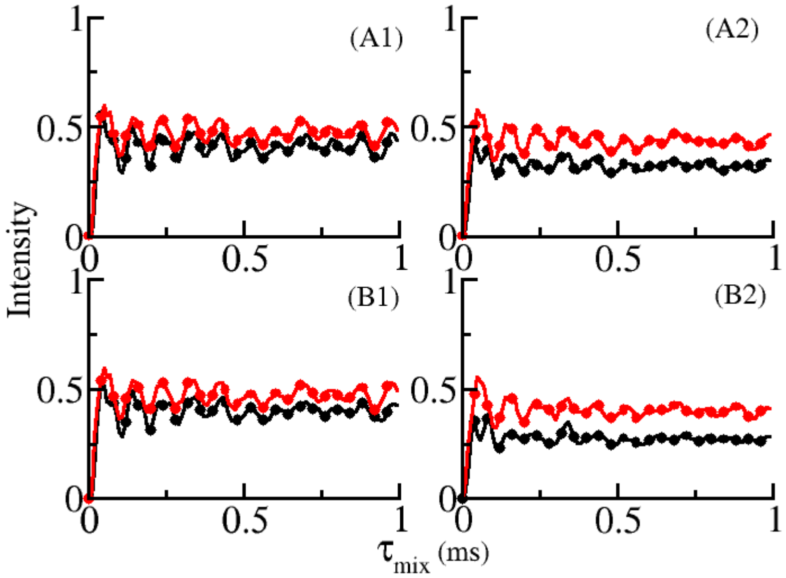

FIGURE 4. PLOT OF INTENSITY VS MIXING TIME.

It is a mixing time plot for static Hartmann-Hahn CP for the system of ^{1}H and ^{13}C. Where black curve (——) is for RF field of 10 KHz and red curve (———) is for RF field of 20 KHz on both proton and carbon channels. Panels A1 and A2 are at 500 MHz, while B1 and B2 are at 700 MHz. A1 and B1 correspond to transfer of polarization from ^{1}H to aliphatic carbon. A2 and B2 correspond to polarization transfer from ^{1}H to carbonyl carbon. Solid curve depicts numerical simulations, while dot represents analytical simulations

Chapter 3

Nuclei with spin quantum number $I > 1/2$ are termed as quadrupolar nuclei and possess a non-zero quadrupolar moment as described in section 1.2.6 (of chapter 1). The spin Hamiltonian for a quadrupolar system is represented by [13-19],

$$H = H_Z + H_{RF} + H_Q\,, \tag{3.1}$$

where, H_Z and H_{RF} are identical to our earlier description. H_Q denotes the quadrupolar interaction and is represented in the principal axis frame (PAS) by,

$$H_Q = \frac{\omega_Q}{6}\{(3I_z^2 - I^2) + \frac{\eta}{2}(I_+^2 + I_-^2)\} \tag{3.2}$$

where 'ω_Q' is the quadrupolar coupling constant

$$\omega_Q = \frac{3e^2qQ}{2I(2I-1)\hbar} \tag{3.3}$$

Since, H_Z and H_{RF} are defined in the lab frame, the quadrupolar Hamiltonian defined in the principal axis frame is transformed to the lab frame via Wigner rotation matrices [14-17]. In the lab frame, parts of the quadrupolar Hamiltonian that commute with H_Z are retained as first order quadrupolar Hamiltonian.

In the lab frame the first order quadrupolar interaction is represented by,

$$H_Q^{(1)} = \frac{\omega_Q(\alpha,\beta,\gamma)}{6}\{3I_z^2 - I^2\} \tag{3.3}$$

where the coupling constant depends on the Euler angles relating the PAS to the LAS (lab frame) [14-16].

The second order interaction terms comprise of the single-quantum and double-quantum operators and are often negligible at higher magnetic field strengths.

$$H_Q^{(2)} \propto \{I_+^2 + I_-^2\} + \{I_Z I_+ + I_+ I_Z\} + \{(I_Z I_- + I_- I_Z)\} \quad (3.4)$$

From eqns. (3.1), (3.2), the overall Hamiltonian for a quadrupolar system (to first order) is represented by,

$$H = -\hbar\omega_0 I_z - 2\hbar\omega_1 \cos(\omega_{rf} t).I_x + \frac{\omega_Q(\alpha,\beta,\gamma)}{6}\{(3I_z^2 - I^2) \quad (3.5)$$

In the following sections, we describe the spin dynamics of integer and half-integer quadrupolar spins. For the purpose of illustration, we confine our discussion to *I* = 1, 3/2, 5/2 spin systems.

3.1 Description of quadrupolar spins

3.1.1 Spin *I* = 1

Based on our earlier description the spin *I* = 1 system has three states in the $|I,m\rangle$ basis i.e. $|1,1\rangle$, $|1,0\rangle$, $|1,-1\rangle$. In the presence of an external magnetic field the degeneracy is lifted resulting in the following energy levels.

$$\omega_0 I_z |1\ 1\rangle = -\omega_0 |1\ 1\rangle \quad (3.6a)$$

$$\omega_0 I_z |1\ \text{-}1\rangle = \omega_0 |1\ \text{-}1\rangle \quad (3.6b)$$

$$\omega_0 I_z |1\ 0\rangle = 0 \quad (3.6c)$$

In the absence of quadrupolar interaction, the NMR spectrum for spin *I* = 1 system, will result in a single peak. This condition is often obtained in an isotropic liquid sample.

Including first order quadrupolar interaction:

However, in the presence of first order quadrupolar interaction, the energy levels described above are rearranged as given below,

$$H|1\ 1\rangle = \left[-\omega_0\hbar + \frac{\omega_Q}{6}\right]|1\ 1\rangle \tag{3.7a}$$

$$H|1\ \text{-}1\rangle = \left[\omega_0\hbar + \frac{\omega_Q}{6}\right]|1\ \text{-}1\rangle \tag{3.7b}$$

$$H|1\ 0\rangle = \left[-\frac{\omega_Q}{3}\right]|1\ 0\rangle \tag{3.7c}$$

For a typical I = 1 system, the NMR spectrum comprises of two peaks corresponding to the following transitions:

$$|1,1\rangle \rightarrow |1,0\rangle,$$

$$|1,0\rangle \rightarrow |1,-1\rangle$$

In the case of anisotropic liquid crystals, the quadrupolar splitting gets averaged due to

molecular motions. However in case of solids, depending on the orientation of electric field gradient tensor with respect to external magnetic field, the observed quadrupolar splitting varies. In a powdered sample, the NMR spectrum is broadened due to spatial anisotropy [14-19].

Below, the energy level diagram for the I = 1 system including the first order quadrupolar interaction is presented.

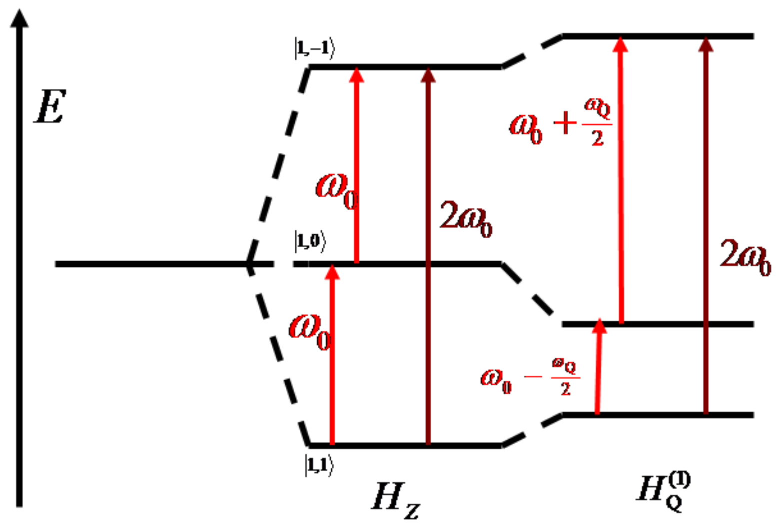

FIGURE 5. SPLITTING OF ENERGY LEVELS FOR SPIN I = 1 SYSTEM.

3.1.2 Spin *I* = 3/2

In the case of spin I = 3/2 system (^{7}Li, ^{23}Na, ^{29}K, ^{35}Ca, ^{37}Ca, ^{79}Br, ^{81}Br, ^{69}Ga, ^{71}Ga, ^{75}As, ^{63}Cu, ^{65}Cu, ^{11}B, ^{179}Au etc.) there are four states, $\left|\frac{3}{2},\frac{3}{2}\right\rangle$, $\left|\frac{3}{2},\frac{1}{2}\right\rangle$, $\left|\frac{3}{2},-\frac{1}{2}\right\rangle$, $\left|\frac{3}{2},-\frac{3}{2}\right\rangle$, in the absence of quadrupolar interactions, the energies of four states in the presence of external magnetic field are given below.

$$\omega_0 I_z \left|\frac{3}{2},\pm\frac{3}{2}\right\rangle = \mp\frac{3}{2}\omega_0 \left|\frac{3}{2},\pm\frac{3}{2}\right\rangle \tag{3.8a}$$

$$\omega_0 I_z \left|\frac{3}{2},\pm\frac{1}{2}\right\rangle = \mp\frac{1}{2}\omega_0 \left|\frac{3}{2},\pm\frac{1}{2}\right\rangle \tag{3.8b}$$

Including first order quadrupolar interaction:

In the presence of first order quadrupolar interaction the Hamiltonian is given by,

$$H = -\hbar\omega_0 I_z + \frac{\omega_Q}{6}\{3I_z^2 - I^2\} \tag{3.9}$$

and the energy levels are rearranged as represented below,

$$H\left|\frac{3}{2},\pm\frac{3}{2}\right\rangle = \left[\mp\frac{3}{2}\omega_0\hbar + \frac{\omega_Q}{2}\right]\left|\frac{3}{2},\pm\frac{3}{2}\right\rangle \tag{3.10a}$$

$$H\left|\frac{3}{2},\pm\frac{1}{2}\right\rangle = \left[\mp\frac{1}{2}\omega_0\hbar - \frac{\omega_Q}{2}\right]\left|\frac{3}{2},\pm\frac{1}{2}\right\rangle \tag{3.10b}$$

In contrast to spin I = 1 system, the NMR spectrum of half integer spins (I = 3/2) comprises of satellite and central transitions.

The satellite transitions are associated with the states,

$$\left.\begin{array}{l}\left|\frac{3}{2},\frac{3}{2}\right\rangle \rightarrow \left|\frac{3}{2},\frac{1}{2}\right\rangle \\ \left|\frac{3}{2},-\frac{1}{2}\right\rangle \rightarrow \left|\frac{3}{2},-\frac{3}{2}\right\rangle\end{array}\right\} \Rightarrow \text{Satellite transitions}$$

While the unique central transition is associated with,

$$\left.\left|\frac{3}{2},\frac{1}{2}\right\rangle \rightarrow \left|\frac{3}{2},-\frac{-1}{2}\right\rangle\right\} \Rightarrow \text{Central transition}$$

Below, we depict the possible transitions and frequencies in a spin I = 3/2 system under the influence of first order quadrupolar interaction.

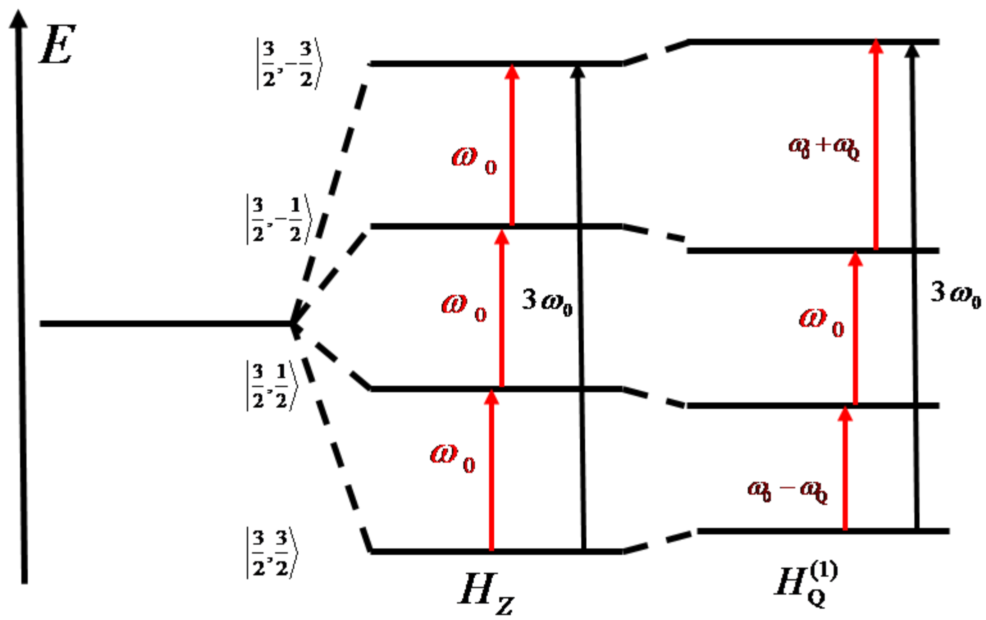

FIGURE 6. ENERGY LEVEL SPLITTING FOR SPIN $I = 3/2$ SYSTEM.

3.1.3 Spin I = 5/2

Analogous to our earlier description, spin I = 5/2 system (^{17}O, ^{25}Mg, ^{27}Al, ^{55}Mn, ^{127}I etc) is represented by six states i.e. $\left|\frac{5}{2},\frac{5}{2}\right\rangle$, $\left|\frac{5}{2},\frac{3}{2}\right\rangle$, $\left|\frac{5}{2},\frac{1}{2}\right\rangle$, $\left|\frac{5}{2},-\frac{1}{2}\right\rangle$, $\left|\frac{5}{2},-\frac{3}{2}\right\rangle$, $\left|\frac{5}{2},-\frac{5}{2}\right\rangle$.

In the presence of first order quadrupolar interaction, the six energy levels are rearranged as represented below,

$$H\left|\frac{5}{2},\pm\frac{5}{2}\right\rangle=\left[\mp\frac{5}{2}\omega_0\hbar+\frac{5}{3}\omega_Q\right]\left|\frac{5}{2},\pm\frac{5}{2}\right\rangle \quad (3.11a)$$

$$H\left|\frac{5}{2},\pm\frac{3}{2}\right\rangle=\left[\mp\frac{3}{2}\omega_0\hbar-\frac{1}{3}\omega_Q\right]\left|\frac{5}{2},\pm\frac{3}{2}\right\rangle \quad (3.11b)$$

$$H\left|\frac{5}{2},\pm\frac{1}{2}\right\rangle=\left[\mp\frac{1}{2}\omega_0\hbar-\frac{4}{3}\omega_Q\right]\left|\frac{5}{2},\pm\frac{1}{2}\right\rangle \quad (3.11c)$$

In contrast to spin I = 3/2 system, there are two sets of satellite transitions besides a central transition.

$$\left.\begin{array}{l}\left|\frac{5}{2},\frac{5}{2}\right\rangle\rightarrow\left|\frac{5}{2},\frac{3}{2}\right\rangle\\ \left|\frac{5}{2},-\frac{3}{2}\right\rangle\rightarrow\left|\frac{5}{2},-\frac{5}{2}\right\rangle\end{array}\right\}\Rightarrow \text{ one set of Satellite transitions}$$

$$\left.\begin{array}{l}\left|\frac{5}{2},\frac{3}{2}\right\rangle \rightarrow \left|\frac{5}{2},\frac{1}{2}\right\rangle \\ \left|\frac{5}{2},-\frac{1}{2}\right\rangle \rightarrow \left|\frac{5}{2},-\frac{3}{2}\right\rangle\end{array}\right\} \Rightarrow \text{ second set of Satellite transitions}$$

$$\left|\frac{5}{2},\frac{1}{2}\right\rangle \rightarrow \left|\frac{5}{2},-\frac{-1}{2}\right\rangle \Big\} \Rightarrow \text{ Central transition}$$

The transitions and frequencies associated with single quantum excitations for spin $I = 5/2$ system, is depicted in Fig. 8.

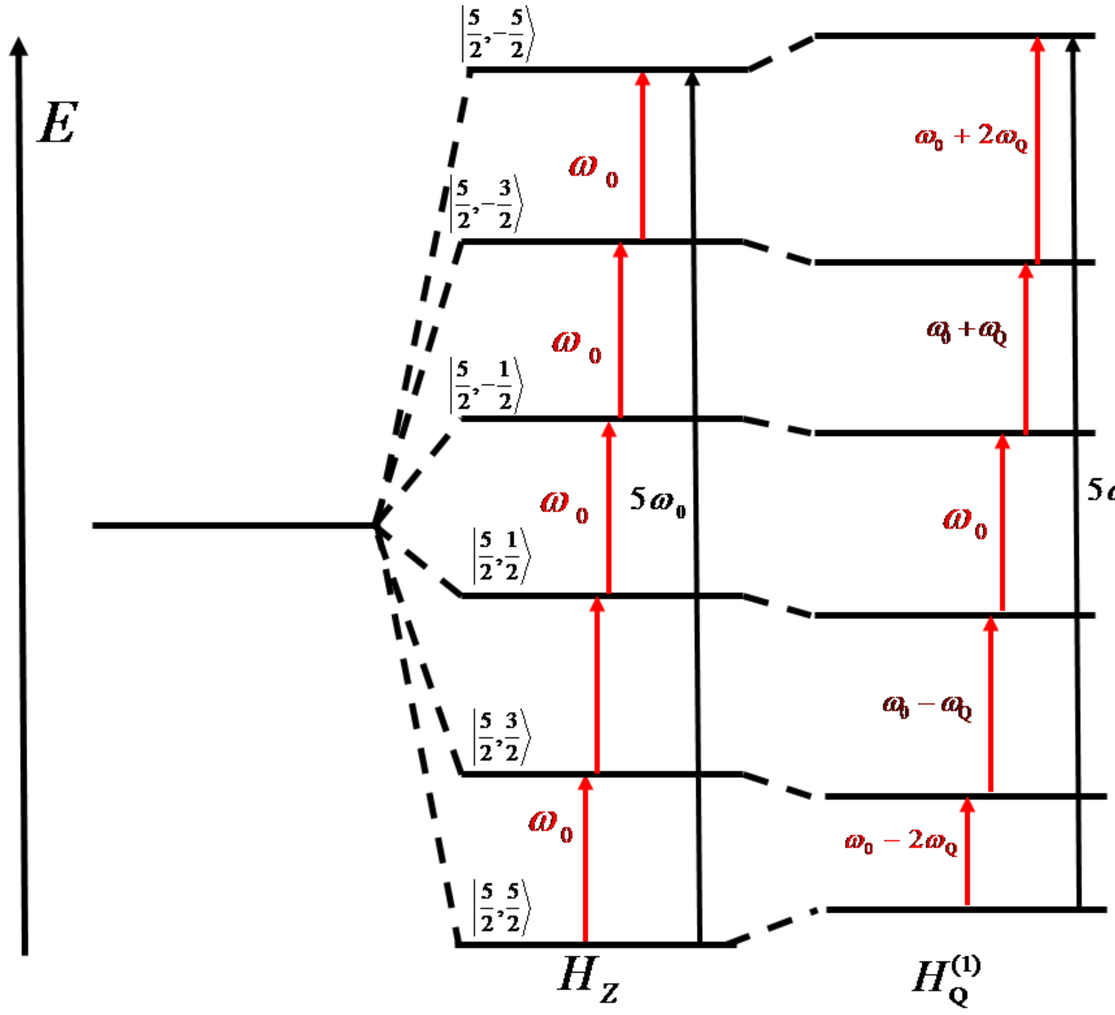

FIGURE 7. ENERGY LEVEL SPLITTING FOR SPIN I = 5/2 SYSTEM

3.2 RF Pulse description

3.2.1 Outline

Our objective is to derive an effective Hamiltonian that describes the effect of an RF pulse (See Figure 4) on the spin system. To demonstrate this aspect, effective RF Hamiltonians are proposed for I = 1, 3/2, 5/2 spin systems (as described in section 3.2.1.1). Employing the effective Hamiltonians, the density operator after the pulse is evaluated and an analytic expression for the time-domain signal is derived.

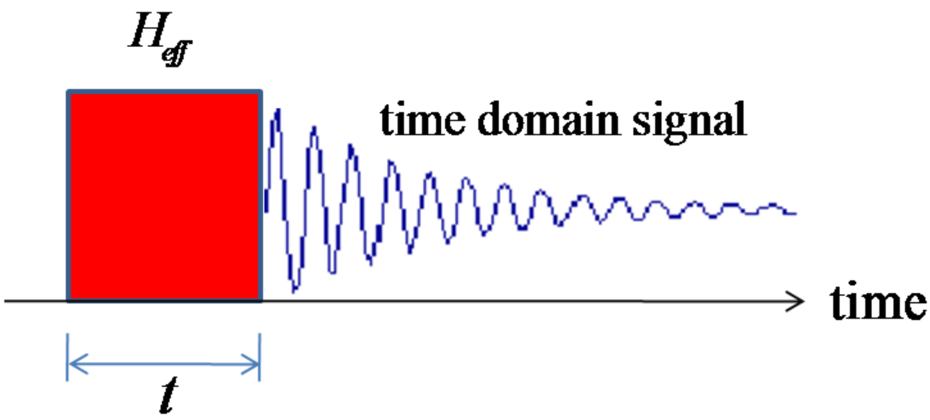

FIGURE 8. PULSE SEQUENCE FOR A SINGLE PULSE EXPERIMENT

3.2.1.1 Effective RF Hamiltonian

The Hamiltonian for a quadrupolar system, in the presence of only first order quadrupolar interaction is represented by,

$$H = -\hbar\omega_0 I_z - 2\hbar\omega_1 \cos(\omega_{rf} t).I_x + \frac{\omega_Q}{6}\{3I_z^2 - I^2\} \tag{3.12}$$

Since the magnitude of Zeeman interaction and quadrupolar interaction is quite large compared to the magnitude of RF amplitude, it is necessary to get rid of the Zeeman and quadrupolar interactions using unitary transformations.

To beginwith, the transformation in to the quadrupolar interaction frame is defined by,

$$U_1 = \exp\left\{ i\frac{\omega_Q}{6}(3I_z^2 - I^2)t \right\} \tag{3.13}$$

In this frame the Hamiltonian '*H*' [see eqn. (3.12)] is transformed as represented below,

$$\tilde{H} = \exp\left\{i\frac{\omega_Q}{6}(3I_z^2 - I^2)t\right\} H \exp\left\{-i\frac{\omega_Q}{6}(3I_z^2 - I^2)t\right\} \tag{3.14}$$

$$\tilde{H} = \exp\left\{i\frac{\omega_Q}{6}(3I_z^2 - I^2)t\right\}[-\hbar\omega_0 I_z - 2\hbar\omega_1\cos(\omega_{rf}t).I_x + \frac{\omega_Q}{6}\{3I_z^2 - I^2\}]\exp\left\{-i\frac{\omega_Q}{6}(3I_z^2 - I^2)t\right\} \tag{3.15}$$

In the quadrupolar interaction frame, the Zeeman Hamiltonian ($H_Z = -\hbar\omega_0 I_Z$) is invariant $\left(\text{i.e. } \left[I_z,(3I_z^2 - I^2)\right] = 0\right)$. However, the RF Hamiltonian is transformed and is evaluated employing the BCH formula given below,

$$\tilde{H} = I_x + \left[(3I_z^2 - I^2), I_x\right](i\phi t) + \left[(3I_z^2 - I^2),\left[(3I_z^2 - I^2), I_x\right]\right]\frac{(i\phi t)^2}{2!} + \left[(3I_z^2 - I^2),\left[(3I_z^2 - I^2),\left[(3I_z^2 - I^2)I_x\right]\right]\right]\frac{(i\phi t)^3}{3!} + ... \tag{3.16}$$

To evaluate this expression, we express the operators in terms of matrices. Then employing the matrix algebra closed form solution for (3.16) is obtained.

The transformation into the Zeeman interaction frame is defined by,

$$U_2 = \exp(-i\omega_0 t I_z) \tag{3.17}$$

The Hamiltonian in the Zeeman interaction frame results in the effective RF Hamiltonian.

As described earlier, the detection operator (say I^+), and the initial density matrix '$\rho(0)$' are transformed identically by the two unitary transformations described above.

Since, $\left[\rho(0), U_1\right] = 0$, $\left[\rho(0), U_2\right] = 0$, the initial density operator is invariant. However the detection operator is transformed analogous to the RF Hamiltonian.

3.2.1.2 Evolution of density matrix under effective Hamiltonian

Simultaneously the time evolution of the density matrix is obtained by solving Liouville equation of motion,

$$i\hbar\frac{d\rho(t)}{dt} = \left[H, \rho(t)\right] \tag{3.18}$$

Since, the Hamiltonian is time independent, the final solution for above Liouville equation is represented by,

$$\rho(t) = \exp\left\{\frac{i}{\hbar}Ht\right\}\rho(0)\exp\left\{-\frac{i}{\hbar}Ht\right\} \tag{3.19}$$

and is simplified by employing BCH expansion given below,

$$\exp\left\{\frac{i}{\hbar}Ht\right\}\rho(0)\exp\left\{-\frac{i}{\hbar}Ht\right\} = \rho(0) + \left(\frac{i}{\hbar}t\right)\left[H,\rho(0)\right] + \frac{1}{2!}\left(\frac{i}{\hbar}t\right)^2\left[H,\left[H,\rho(0)\right]\right] + \ldots \tag{3.20}$$

$$\Rightarrow \rho(t) = \rho(0) + \left(\frac{i}{\hbar}t\right)\left[H,\rho(0)\right] + \frac{1}{2!}\left(\frac{i}{\hbar}t\right)^2\left[H,\left[H,\rho(0)\right]\right] + \ldots.. \tag{3.21}$$

Subsequently, the time domain signal is obtained, by evaluating the trace of evolved density matrix and the transformed detection operator.

$$\langle D\rangle = Tr\left[\rho(t).\tilde{\tilde{D}}_+\right] \tag{3.22}$$

Based on the above formalism, we present an analytical description of pulses in I = 1, I = 3/2, I = 5/2 systems in the following sections.

3.2.2 *I* = 1 System

3.2.2.1 Effective RF Hamiltonian for *I* = 1 system

Quadrupole interaction frame transformation: The Hamiltonian in the quadrupolar interaction frame [for detail see eqn. (4) of appendix 1] defined by $U_1 = \exp\left\{i\frac{\omega_Q}{6}(3I_z^2 - I^2)t\right\}$ and is represented by,

$$\tilde{H} = -\hbar\omega_0 I_Z + \frac{1}{2}\left\{iSin\left(\frac{\omega_Q}{2}t\right)\begin{bmatrix} 0 & \sqrt{2} & 0 \\ -\sqrt{2} & 0 & -\sqrt{2} \\ 0 & \sqrt{2} & 0 \end{bmatrix} + Cos\left(\frac{\omega_Q}{2}t\right)\begin{bmatrix} 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & \sqrt{2} \\ 0 & \sqrt{2} & 0 \end{bmatrix}\right\}\left\{-2\hbar\omega_1\cos(\omega_{rf}t)\right\} \tag{3.23}$$

Zeeman interaction frame transformation: The Hamiltonian in the Zeeman interaction frame, defined by $U_2 = \exp(-i\omega_0 t I_z)$, is represented [for detail see eqn. (8) of appendix 1] by,

$$\tilde{\tilde{H}} = \left\{ \begin{array}{l} iSin\left(\frac{\omega_Q}{2}t\right)\left(\begin{bmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & -\sqrt{2} \\ 0 & 0 & 0 \end{bmatrix}\exp(i\omega_0 t) + \begin{bmatrix} 0 & 0 & 0 \\ -\sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{bmatrix}\exp(-i\omega_0 t)\right) \\ +Cos\left(\frac{\omega_Q}{2}t\right)\left(\begin{bmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{bmatrix}\exp(i\omega_0 t) + \begin{bmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{bmatrix}\exp(-i\omega_0 t)\right) \end{array} \right\} \left\{-\hbar\omega_1 \cos(\omega_{rf} t)\right\}$$

(3.24)

Employing trigonometric identities and combining like coefficients, the above expression [eqn. (3.24)] is simplified and re-expressed below,

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2} \left\{ \begin{array}{l} \left\{ \frac{e^{i(\omega_{rf}+\omega_0+\frac{\omega_Q}{2})t} + e^{i(-\omega_{rf}+\omega_0+\frac{\omega_Q}{2})t}}{2} - \frac{e^{i(\omega_{rf}+\omega_0-\frac{\omega_Q}{2})t} + e^{i(-\omega_{rf}+\omega_0-\frac{\omega_Q}{2})t}}{2} \right\} \begin{bmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & -\sqrt{2} \\ 0 & 0 & 0 \end{bmatrix} \\ + \left\{ \frac{e^{i(\omega_{rf}-\omega_0+\frac{\omega_Q}{2})t} + e^{i(-\omega_{rf}-\omega_0+\frac{\omega_Q}{2})t}}{2} - \frac{e^{i(\omega_{rf}-\omega_0-\frac{\omega_Q}{2})t} + e^{i(-\omega_{rf}-\omega_0-\frac{\omega_Q}{2})t}}{2} \right\} \begin{bmatrix} 0 & 0 & 0 \\ -\sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{bmatrix} \\ + \left\{ \frac{e^{i(\omega_{rf}+\omega_0+\frac{\omega_Q}{2})t} + e^{i(-\omega_{rf}+\omega_0+\frac{\omega_Q}{2})t}}{2} + \frac{e^{i(\omega_{rf}+\omega_0-\frac{\omega_Q}{2})t} + e^{i(-\omega_{rf}+\omega_0-\frac{\omega_Q}{2})t}}{2} \right\} \begin{bmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{bmatrix} \\ + \left\{ \frac{e^{i(\omega_{rf}-\omega_0+\frac{\omega_Q}{2})t} + e^{i(-\omega_{rf}-\omega_0+\frac{\omega_Q}{2})t}}{2} + \frac{e^{i(\omega_{rf}-\omega_0-\frac{\omega_Q}{2})t} + e^{i(-\omega_{rf}-\omega_0-\frac{\omega_Q}{2})t}}{2} \right\} \begin{bmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{bmatrix} \end{array} \right\}$$

(3.25)

It is important here to realize that the above expression [eqn. (3.25)] has been obtained after invoking the secular approximation (high frequency terms are neglected).

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\left\{\begin{array}{l}\left\{\frac{e^{i(-\omega_{rf}+\omega_0+\frac{\omega_Q}{2})t}}{2} - \frac{e^{i(-\omega_{rf}+\omega_0-\frac{\omega_Q}{2})t}}{2}\right\}\begin{bmatrix}0 & \sqrt{2} & 0\\ 0 & 0 & -\sqrt{2}\\ 0 & 0 & 0\end{bmatrix} + \left\{\frac{e^{i(\omega_{rf}-\omega_0+\frac{\omega_Q}{2})t}}{2} - \frac{e^{i(\omega_{rf}-\omega_0-\frac{\omega_Q}{2})t}}{2}\right\}\begin{bmatrix}0 & 0 & 0\\ -\sqrt{2} & 0 & 0\\ 0 & \sqrt{2} & 0\end{bmatrix}\\ + \left\{\frac{e^{i(-\omega_{rf}+\omega_0+\frac{\omega_Q}{2})t}}{2} + \frac{e^{i(-\omega_{rf}+\omega_0-\frac{\omega_Q}{2})t}}{2}\right\}\begin{bmatrix}0 & \sqrt{2} & 0\\ 0 & 0 & \sqrt{2}\\ 0 & 0 & 0\end{bmatrix} + \left\{\frac{e^{i(\omega_{rf}-\omega_0+\frac{\omega_Q}{2})t}}{2} + \frac{e^{i(\omega_{rf}-\omega_0-\frac{\omega_Q}{2})t}}{2}\right\}\begin{bmatrix}0 & 0 & 0\\ \sqrt{2} & 0 & 0\\ 0 & \sqrt{2} & 0\end{bmatrix}\end{array}\right\} \tag{3.26}$$

For a given magnetic field strength 'B_0', depending on the relative magnitude of the quadrupolar coupling (ω_Q) and RF amplitude (ω_{rf}), selective and non-selective transitions could be induced.

The non-selective experiments are commonly known as hard pulse experiments and are commonly employed to excite all the transitions. Thus, all the exponential terms become unity and resulting in an effective RF Hamiltonian corresponding to **hard pulse regime** represented by the I_x operator,

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\begin{bmatrix}0 & \sqrt{2} & 0\\ \sqrt{2} & 0 & \sqrt{2}\\ 0 & \sqrt{2} & 0\end{bmatrix} \tag{3.27}$$

By contrast, in the case of selective excitations (called soft pulse experiments) there are two possible transitions given below,

$$\text{Case 1} \Rightarrow \quad \omega_{rf} = \left(\omega_0 - \frac{\omega_Q}{2}\right) \tag{3.28a}$$

$$\text{Case 2} \Rightarrow \quad \omega_{rf} = \left(\omega_0 + \frac{\omega_Q}{2}\right) \tag{3.28b}$$

When the frequency of the RF pulse is such that, $\omega_{rf} = \left(\omega_0 - \frac{\omega_Q}{2}\right)$ the effective RF Hamiltonian under secular approximation is represented by,

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\left\{\left\{-\frac{1}{2}\right\}\begin{bmatrix}0 & \sqrt{2} & 0\\ 0 & 0 & -\sqrt{2}\\ 0 & 0 & 0\end{bmatrix} + \left\{\frac{1}{2}\right\}\begin{bmatrix}0 & 0 & 0\\ -\sqrt{2} & 0 & 0\\ 0 & \sqrt{2} & 0\end{bmatrix} + \left\{\frac{1}{2}\right\}\begin{bmatrix}0 & \sqrt{2} & 0\\ 0 & 0 & \sqrt{2}\\ 0 & 0 & 0\end{bmatrix} + \left\{\frac{1}{2}\right\}\begin{bmatrix}0 & 0 & 0\\ \sqrt{2} & 0 & 0\\ 0 & \sqrt{2} & 0\end{bmatrix}\right\}$$

which finally results in,

$$\Rightarrow \quad \tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\begin{bmatrix}0 & 0 & 0\\ 0 & 0 & \sqrt{2}\\ 0 & \sqrt{2} & 0\end{bmatrix} \qquad (3.29)$$

In a similar vein, for $\omega_{rf} = \left(\omega_0 + \frac{\omega_Q}{2}\right)$, the effective Hamiltonian is represented by,

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\left\{\left\{\frac{1}{2}\right\}\begin{bmatrix}0 & \sqrt{2} & 0\\ 0 & 0 & -\sqrt{2}\\ 0 & 0 & 0\end{bmatrix} + \left\{-\frac{1}{2}\right\}\begin{bmatrix}0 & 0 & 0\\ -\sqrt{2} & 0 & 0\\ 0 & \sqrt{2} & 0\end{bmatrix} + \left\{\frac{1}{2}\right\}\begin{bmatrix}0 & \sqrt{2} & 0\\ 0 & 0 & \sqrt{2}\\ 0 & 0 & 0\end{bmatrix} + \left\{\frac{1}{2}\right\}\begin{bmatrix}0 & 0 & 0\\ \sqrt{2} & 0 & 0\\ 0 & \sqrt{2} & 0\end{bmatrix}\right\}$$

and reduces to,

$$\Rightarrow \tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\begin{bmatrix}0 & \sqrt{2} & 0\\ \sqrt{2} & 0 & 0\\ 0 & 0 & 0\end{bmatrix} \qquad (3.30)$$

3.2.2.2 Detection operator

The detection operator ‘ I^+ ’ operator and is represented in matrix form as:

$$I^+ = \begin{bmatrix}0 & \sqrt{2} & 0\\ 0 & 0 & \sqrt{2}\\ 0 & 0 & 0\end{bmatrix} \qquad (3.31)$$

$D = N^2 i I^+$

where, $N = \frac{1}{\sqrt{2}}$

The detection operator in the effective interaction frame is represented by,

$$\tilde{\tilde{I}}^+ = iSin\left(\frac{\omega_Q}{2}t\right)\begin{bmatrix}0 & \sqrt{2} & 0\\ 0 & 0 & -\sqrt{2}\\ 0 & 0 & 0\end{bmatrix}\exp(i\omega_0 t) + Cos\left(\frac{\omega_Q}{2}t\right)\begin{bmatrix}0 & \sqrt{2} & 0\\ 0 & 0 & \sqrt{2}\\ 0 & 0 & 0\end{bmatrix}\exp(i\omega_0 t) \qquad (3.32)$$

3.2.2.3 Evolution of density matrix

The density operator after the pulse is represented by,

$$\rho(t)=\rho(0)+\left(\frac{i}{\hbar}t\right)[H,\rho(0)]+\frac{1}{2!}\left(\frac{i}{\hbar}t\right)^2[H,[H,\rho(0)]]+.....$$

where, $\rho(0)=\begin{bmatrix}1&0&0\\0&0&0\\0&0&-1\end{bmatrix}$ (3.33)

Below, we illustrate the two excitations under selective and non-selective regimes.

A) Non-selective excitations

In the case of non-selective excitations, the density matrix after the pulse [for detail see eqn. (9) of appendix 1] is represented by,

$$\Rightarrow\rho(t)=Cos(\omega_1 t)\begin{bmatrix}1&0&0\\0&0&0\\0&0&-1\end{bmatrix}-iSin(\omega_1 t)\frac{1}{2}\begin{bmatrix}0&-\sqrt{2}&0\\\sqrt{2}&0&-\sqrt{2}\\0&\sqrt{2}&0\end{bmatrix} \quad (3.34)$$

The time domain signal is obtained by evaluating [for detail see eqn. (10) of appendix 1] the following equation:

$$\left\langle \tilde{\tilde{I}}^{+}\right\rangle = Tr\left[\rho(t).\tilde{\tilde{I}}^{+}\right] \quad (3.35)$$

which on simplification reduces to,

$$\left\langle \tilde{\tilde{I}}^{+}\right\rangle = 2N^2 Sin(\omega_1 t)\left\{\frac{e^{i\frac{\omega_Q}{2}t+i\omega_0 t}+e^{-i\frac{\omega_Q}{2}t+i\omega_0 t}}{2}\right\} \quad (3.36)$$

From eqn. (3.36), the maximum intensity obtained for time domain signal in non-selective excitations is N^2, when $Sin(\omega_1 t)$ is equal to unity, i.e. $t=\frac{\pi}{2\omega_1}$

B) Selective excitations

As discussed in eqn. (3.28), for a I = 1 system there are two matching conditions corresponding to $\omega_{rf}=\left(\omega_0\pm\frac{\omega_Q}{2}\right)$.

Case 1: The density matrix after the pulse [for detail see eqn. (11) of appendix 1] with frequency, $\omega_{rf}=\left(\omega_0-\frac{\omega_Q}{2}\right)$ is represented by,

$$\rho(t)=\begin{bmatrix}1&0&0\\0&0&0\\0&0&-1\end{bmatrix}-iSin\left(\sqrt{2}\omega_1 t\right)\frac{1}{2}\begin{bmatrix}0&0&0\\0&0&-1\\0&1&0\end{bmatrix}+\left\{Cos\left(\sqrt{2}\omega_1 t\right)-1\right\}\frac{1}{2}\begin{bmatrix}0&0&0\\0&1&0\\0&0&-1\end{bmatrix} \tag{3.37}$$

The time domain signal obtained is represented by,

$$\left\langle \tilde{\tilde{I}}^{+}\right\rangle=\frac{1}{\sqrt{2}}N^2 Sin\left(\sqrt{2}\omega_1 t\right)e^{i\left(\omega_0-\frac{\omega_Q}{2}\right)t} \tag{3.38}$$

From eqn. (3.38), the maximum intensity obtained for time domain signal in this selective excitation case is $\frac{1}{\sqrt{2}}N^2$, when $Sin\left(\sqrt{2}\omega_1 t\right)$ is equal to unity, i.e. $t=\frac{\pi}{2\sqrt{2}\omega_1}$

In a similar vein, the time domain signal for **Case 2**, $\omega_{rf}=\left(\omega_0+\frac{\omega_Q}{2}\right)$, is represented by,

$$\left\langle \tilde{\tilde{I}}^{+}\right\rangle=\frac{1}{\sqrt{2}}N^2 Sin\left(\sqrt{2}\omega_1 t\right)e^{i\left(\omega_0+\frac{\omega_Q}{2}\right)t} \tag{3.39}$$

From eqn. (3.39), the maximum intensity obtained for time domain signal in this selective excitation case is $\frac{1}{\sqrt{2}}N^2$, when $Sin\left(\sqrt{2}\omega_1 t\right)$ is equal to unity, i.e. $t=\frac{\pi}{2\sqrt{2}\omega_1}$

Below, we summarize the final results for the spin *I* = 1 system.

Table 1. Summary of spin *I* = 1 results.

S.No.	Matching Condition	Frequency	Intensity	Pulse duration
1	$\omega_{rf}=\omega_0+\frac{\omega_Q}{2}$	$\omega_0+\frac{\omega_Q}{2}$	$\frac{1}{\sqrt{2}}N^2$	$\frac{\pi}{2\sqrt{2}\omega_1}$
2	$\omega_{rf}=\omega_0-\frac{\omega_Q}{2}$	$\omega_0-\frac{\omega_Q}{2}$	$\frac{1}{\sqrt{2}}N^2$	$\frac{\pi}{2\sqrt{2}\omega_1}$
3	Hard pulse	Both frequencies	N^2, N^2	$\frac{\pi}{2\omega_1}$

In table 1, value of *N* for spin *I* =1 is $\frac{1}{\sqrt{2}}$.

Below, we present the numerically simulated spectrum of spin *I* = 1, for varying symmetries (η = 0, 0.5, 1). The numerical simulations presented correspond to a powdered sample and comprise of 6044 orientations. Employing the analytic expression for the time-domain signal and subsequent Fourier transformation, the frequency domain spectrum is obtained using a numerical code in FORTRAN.

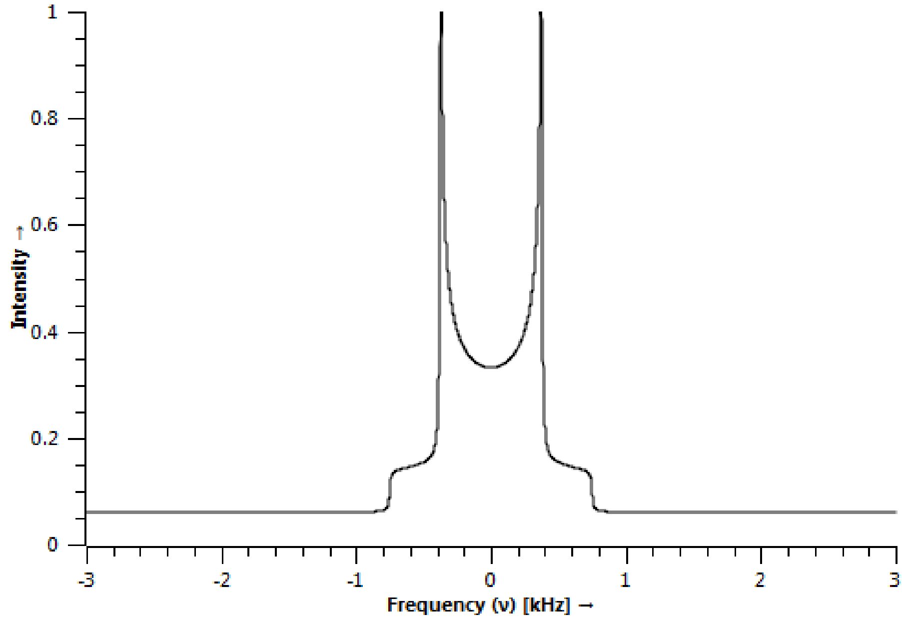

FIGURE 9(A). POWDER AVERAGED SPECTRUM OF SPIN I = 1, WITH η =0

This is a hard pulse (π/2) spectrum for ^{14}N nuclei (spin I = 1) acquired over 6044 orientations, with quadrupolar constant, ω_Q = 3/4 KHz, and C_Q = 1 KHz. ω_Q = 3/4 KHz, and C_Q = 1 KHz.

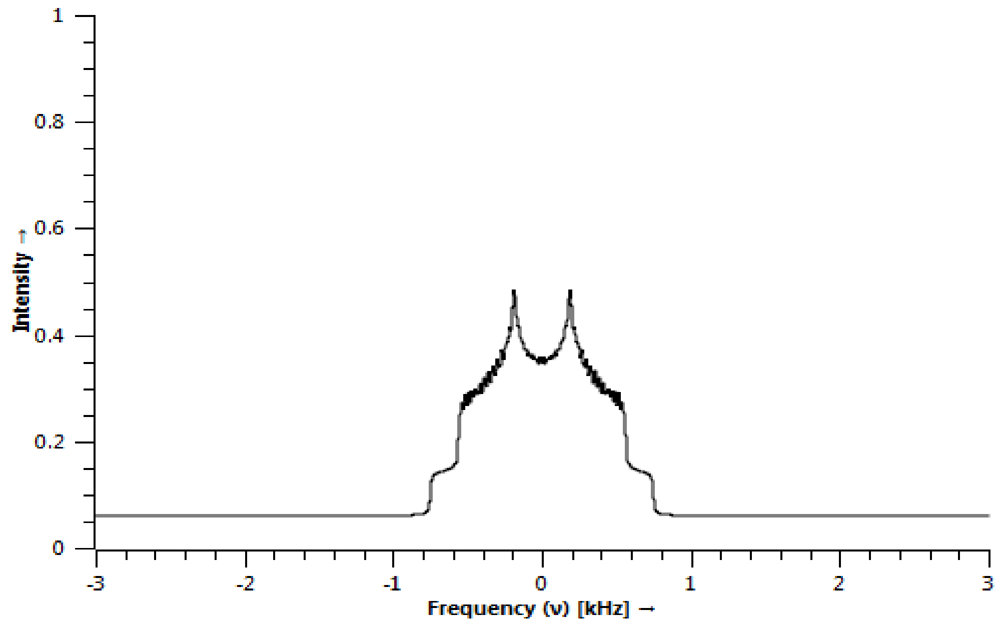

FIGURE 9(B). POWDER AVERAGED SPECTRUM OF SPIN I = 1, WITH η =0.5.

This is a hard pulse (π/2) spectrum for ^{14}N nuclei (spin I = 1) acquired over 6044 orientations, with quadrupolar constant, ω_Q = 3/4 KHz, and C_Q = 1 KHz.

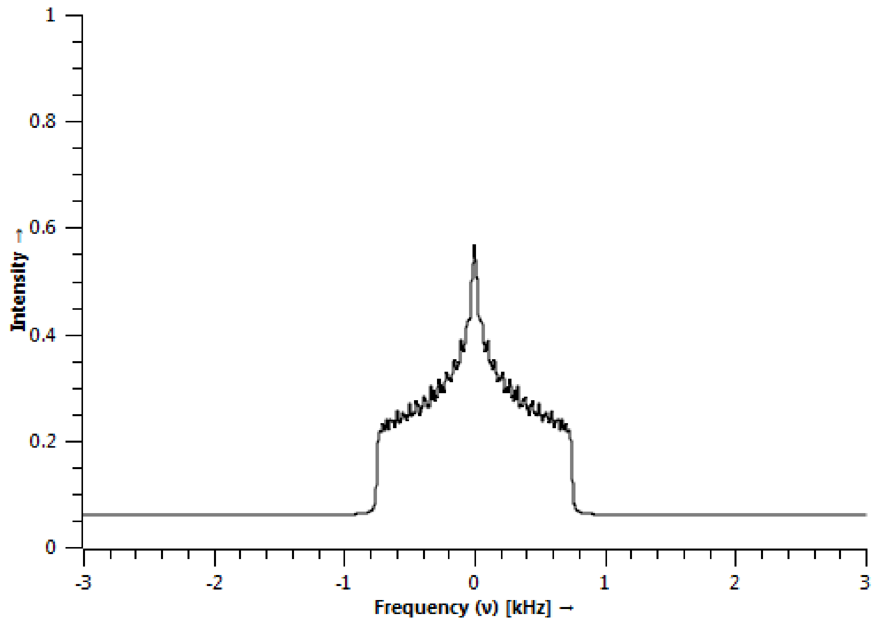

FIGURE 9(C). POWDER AVERAGED SPECTRUM OF SPIN I = 1, WITH η =1

This is a hard pulse (π/2) spectrum for ^{14}N nuclei (spin I = 1) acquired over 6044 orientations, with quadrupolar constant, ω_Q = 3/4 KHz, and C_Q = 1 KHz.

3.2.3 *I* = 3/2 System

Following the description in the earlier sections, the Hamiltonian for spin *I* = 3/2 in the quadrupolar interaction frame and Zeeman interaction frame is represented in eqn. (3.40) and (3.41) respectively [for details see appendix 2].

$$\tilde{H} = -\hbar\omega_0 I_Z + \left\{ \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + iSin(\omega_Q t) \begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix} + Cos(\omega_Q t) \begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix} \right\} \left\{ -\hbar\omega_1 \cos(\omega_{rf} t) \right\} \tag{3.40}$$

$$\begin{aligned} \tilde{\tilde{H}} = \left\{ -\hbar\omega_1 \cos(\omega_{rf} t) \right\} \Bigg\{ & \left(\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \exp(i\omega_0 t) + \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \exp(-i\omega_0 t) \right) \\ & + iSin(\omega_Q t) \left(\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{3} \\ 0 & 0 & 0 & 0 \end{bmatrix} \exp(i\omega_0 t) + \begin{bmatrix} 0 & 0 & 0 & 0 \\ -\sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix} \exp(-i\omega_0 t) \right) \\ & + Cos(\omega_Q t) \left(\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & 0 & 0 \end{bmatrix} \exp(i\omega_0 t) + \begin{bmatrix} 0 & 0 & 0 & 0 \\ \sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix} \exp(-i\omega_0 t) \right) \Bigg\} \end{aligned} \tag{3.41}$$

Employing secular approximation and equating like terms the effective RF Hamiltonian is represented below,

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\left\{\begin{array}{l} \left\{e^{i(\omega_{rf}-\omega_0)t}\right\}\begin{bmatrix}0&0&0&0\\0&0&2&0\\0&0&0&0\\0&0&0&0\end{bmatrix} + \left\{e^{i(-\omega_{rf}+\omega_0)t}\right\}\begin{bmatrix}0&0&0&0\\0&0&0&0\\0&2&0&0\\0&0&0&0\end{bmatrix} + \\ + \left\{\frac{e^{i(-\omega_{rf}+\omega_0+\omega_Q)t}}{2} - \frac{e^{i(-\omega_{rf}+\omega_0-\omega_Q)t}}{2}\right\}\begin{bmatrix}0&\sqrt{3}&0&0\\0&0&0&0\\0&0&0&-\sqrt{3}\\0&0&0&0\end{bmatrix} + \left\{\frac{e^{i(\omega_{rf}-\omega_0+\omega_Q)t}}{2} - \frac{e^{i(\omega_{rf}-\omega_0-\omega_Q)t}}{2}\right\}\begin{bmatrix}0&0&0&0\\-\sqrt{3}&0&0&0\\0&0&0&0\\0&0&\sqrt{3}&0\end{bmatrix} \\ + \left\{\frac{e^{i(-\omega_{rf}+\omega_0+\omega_Q)t}}{2} + \frac{e^{i(-\omega_{rf}+\omega_0-\omega_Q)t}}{2}\right\}\begin{bmatrix}0&\sqrt{3}&0&0\\0&0&0&0\\0&0&0&\sqrt{3}\\0&0&0&0\end{bmatrix} + \left\{\frac{e^{i(\omega_{rf}-\omega_0+\omega_Q)t}}{2} + \frac{e^{i(\omega_{rf}-\omega_0-\omega_Q)t}}{2}\right\}\begin{bmatrix}0&0&0&0\\\sqrt{3}&0&0&0\\0&0&0&0\\0&0&\sqrt{3}&0\end{bmatrix} \end{array}\right\} \tag{3.42}$$

In the case of the non-selective excitations, the effective RF Hamiltonian depicted in eqn. (3.42) reduces to I_x operator, represented by,

$$\Rightarrow \tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\begin{bmatrix}0&\sqrt{3}&0&0\\\sqrt{3}&0&2&0\\0&2&0&\sqrt{3}\\0&0&\sqrt{3}&0\end{bmatrix} \tag{3.43}$$

In the case of selective excitations, the matching condition corresponds to a set of satellite transition and a central transition.

$$\left.\begin{array}{l}\text{Case 1} \Rightarrow \omega_{rf} = (\omega_0 - \omega_Q)\\ \text{Case 2} \Rightarrow \omega_{rf} = (\omega_0 + \omega_Q)\end{array}\right\} \rightarrow \text{Satellite transition} \tag{3.44a}$$

$$\text{Case 3} \Rightarrow \omega_{rf} = (\omega_0)\} \rightarrow \text{Central transition} \tag{3.44b}$$

The effective RF Hamiltonian for central transition is given by eqn. (3.47), while the effective Hamiltonians for the satellite transitions are represented by eqn. (3.45) and (3.46) respectively.

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix} \tag{3.45}$$

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \tag{3.46}$$

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \tag{3.47}$$

Following the procedure given in the previous sections, the transformed detection operator and the density operator are represented below by eqns. (3.48) and (3.49) respectively.

$$\tilde{\tilde{I}}^{+} = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \exp(i\omega_0 t) + iSin(\omega_Q t)\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{3} \\ 0 & 0 & 0 & 0 \end{bmatrix} \exp(i\omega_0 t) + Cos(\omega_Q t)\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & 0 & 0 \end{bmatrix} \exp(i\omega_0 t) \tag{3.48}$$

$$\tilde{\tilde{\rho}}(0) = \frac{1}{2}\begin{bmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{bmatrix} \tag{3.49}$$

3.2.3.2 Evolution of density matrix

As mentioned in eqn. (3.21), the density operator after the pulse is represented by,

$$\rho(t) = \rho(0) + \left(\frac{i}{\hbar}t\right)\left[H, \rho(0)\right] + \frac{1}{2!}\left(\frac{i}{\hbar}t\right)^2 \left[H, \left[H, \rho(0)\right]\right] + ...$$

A) Non-selective excitations

In the case of non-selective excitation, the density operator [see eqn. (9) of appendix 2] after the pulse is represented by,

$$\rho(t) = Cos\left(\omega_1 t\right)\frac{1}{2}\begin{bmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{bmatrix} - iSin\left(\omega_1 t\right)\frac{1}{2}\begin{bmatrix} 0 & -\sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & -2 & 0 \\ 0 & 2 & 0 & -\sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix} \tag{3.50}$$

and the time domain signal [see eqn. (10) of appendix 2] is represented by eqn. (3.51)

$$\left\langle \tilde{\tilde{I}}^{+} \right\rangle = N^2 Sin\left(\omega_1 t\right)\left\{ 2e^{i\omega_0 t} + 3\frac{e^{i\omega_Q t + i\omega_0 t} + e^{-i\omega_Q t + i\omega_0 t}}{2} \right\} \tag{3.51}$$

From eqn. (3.51), the maximum intensity obtained for time domain signal in non-selective excitations is N^2, when $Sin\left(\omega_1 t\right)$ is equal to unity, i.e. $t = \frac{\pi}{2\omega_1}$

B) Selective excitations

.**Case 1:** When $\omega_{rf} = \left(\omega_0 - \omega_Q\right)$, the density operator after the pulse [see eqn. (11) of appendix 2] is represented by,

$$\rho(t) = \frac{1}{2}\begin{bmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{bmatrix} - iSin\left(\sqrt{3}\omega_1 t\right)\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{bmatrix} + \left\{Cos\left(\sqrt{3}\omega_1 t\right) - 1\right\}\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \tag{3.52}$$

Subsequently the time domain signal [see eqn. (12) of appendix 2] is represented by,

$$\left\langle \tilde{\tilde{I}}^{+} \right\rangle = \frac{\sqrt{3}}{2} N^2 Sin\left(\sqrt{3}\omega_1 t\right) e^{i\omega_0 t - i\omega_Q t} \tag{3.53}$$

From eqn. (3.53), the maximum intensity obtained for time domain signal in this selective excitation case is $\frac{\sqrt{3}}{2}N^2$, when $Sin\left(\sqrt{3}\omega_1 t\right)$ is equal to unity, i.e. $t = \frac{\pi}{2\sqrt{3}\omega_1}$

Case 2: when $\omega_{rf} = \omega_0 + \omega_Q$, the time domain signal is represented by,

$$\left\langle \tilde{\tilde{I}}^{+} \right\rangle = \frac{\sqrt{3}}{2} N^2 Sin\left(\sqrt{3}\omega_1 t\right) e^{i\omega_Q t + i\omega_0 t} \tag{3.54}$$

Similarly, for this case of selective excitation, maximum intensity of time domain signal obtained is $\frac{\sqrt{3}}{2}N^2$, at $t = \frac{\pi}{2\sqrt{3}\omega_1}$.

Case 3: In the case of the central transition ($\omega_{rf} = \omega_0$), the density operator after the pulse [for detail see eqn. (15) of appendix 2] is represented by,

$$\rho(t) = \frac{1}{2}\begin{bmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{bmatrix} - iSin\left(2\omega_1 t\right)\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + \left\{Cos\left(2\omega_1 t\right) - 1\right\}\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \tag{3.55}$$

The resulting time domain signal [see eqn. (16) of appendix 2] is represented by,

$$\left\langle \tilde{\tilde{I}}^{+} \right\rangle = N^2 Sin\left(2\omega_1 t\right)\exp(i\omega_0 t) \tag{3.56}$$

From eqn. (3.56), the maximum intensity obtained for time domain signal of central transition is N^2, when $Sin\left(2\omega_1 t\right)$ is equal to unity, i.e. $t = \frac{\pi}{4\omega_1}$

The results for spin I = 3/2 are tabulated below.

Table 2. Summary of spin *I* = 3/2 results.

S.No.	Matching condition	Frequency	Intensity	Pulse duration
1	$\omega_{rf} = \omega_0 + \omega_Q$	$\omega_0 + \omega_Q$	$\frac{\sqrt{3}}{2}N^2$	$\frac{\pi}{2\sqrt{3}\omega_1}$
2	$\omega_{rf} = \omega_0 - \omega_Q$	$\omega_0 - \omega_Q$	$\frac{\sqrt{3}}{2}N^2$	$\frac{\pi}{2\sqrt{3}\omega_1}$
3	$\omega_{rf} = \omega_0$	ω_0	N^2	$\frac{\pi}{4\omega_1}$
4	Hard pulse	All three frequencies	$2N^2$, $\frac{3}{2}N^2$, $\frac{3}{2}N^2$	$\frac{\pi}{2\omega_1}$

In table 2, value of N is $\frac{1}{\sqrt{5}}$

Below, we are presenting the numerically simulated spectrum of spin I = 3/2, for varying symmetries (η = 0, 0.5, 1). Confirming our formalism spin I = 3/2 spectrum, shows a central band and one set of satellite transitions.

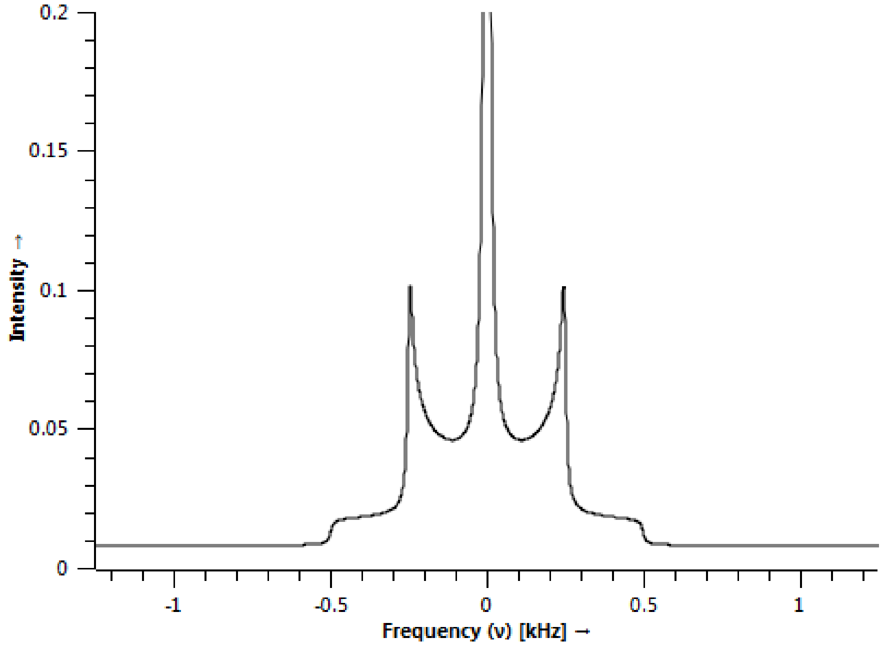

FIGURE 10(A). POWDER AVERAGED SPECTRUM OF SPIN I = 3/2, WITH η=0.

This is a hard pulse (π/2) spectrum for ^{23}Na nuclei (spin I = 3/2) acquired over 6044 orientations, with quadrupolar constant, ω_Q = 2/5 KHz, and C_Q = 1 KHz.

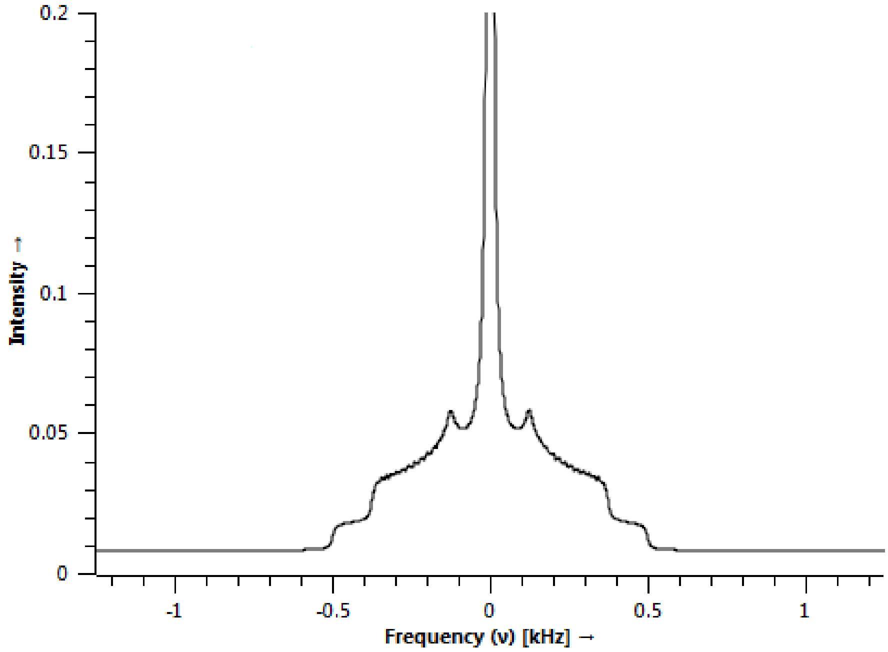

FIGURE 10(B). POWDER AVERAGED SPECTRUM OF SPIN I = 3/2 WITH η=0.5.

This is a hard pulse (π/2) spectrum for ^{23}Na nuclei (spin I = 3/2) acquired over 6044 orientations, with quadrupolar constant, ω_Q = 2/5 KHz, and C_Q = 1 KHz.

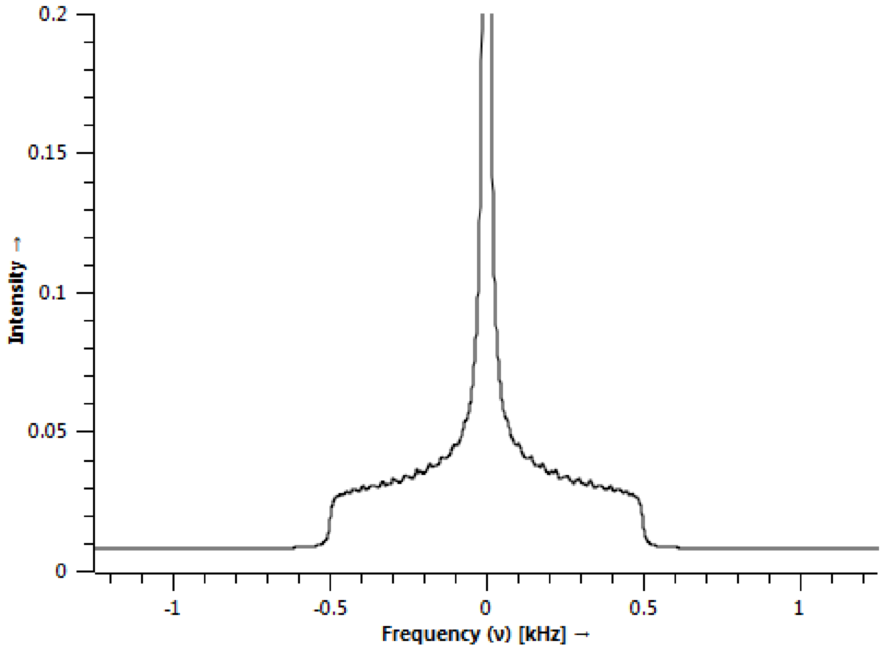

FIGURE 10(C). POWDER AVERAGED SPECTRUM OF SPIN I = 3/2, WITH η=1.0.
This is a hard pulse (π/2) spectrum for ^{23}Na nuclei (spin I = 3/2) acquired over 6044 orientations, with quadrupolar constant, ω_Q = 2/5 KHz and C_Q = 1 KHz.

3.2.4 *I* = 5/2 System

3.2.4.1 Effective RF Hamiltonian

Following the description in the earlier sections, the effective RF Hamiltonian for a spin I = 5/2 system is derived [for detail see eqn. (4) and (8) of appendix 3] and is represented below,

$$
\begin{aligned}
\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\Bigg\{ & \left\{e^{i\left(-\omega_{rf}+\omega_0\right)t}\right\}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&3&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}+\left\{e^{i\left(\omega_{rf}-\omega_0\right)t}\right\}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&3&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix} \\
& +\left\{\frac{e^{i(-\omega_{rf}+\omega_0+2\omega_Q)t}}{2}-\frac{e^{i(-\omega_{rf}+\omega_0-2\omega_Q)t}}{2}\right\}\begin{bmatrix}0&\sqrt{5}&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&-\sqrt{5}\\0&0&0&0&0&0\end{bmatrix}+\left\{\frac{e^{i(\omega_{rf}-\omega_0+2\omega_Q)t}}{2}-\frac{e^{i(\omega_{rf}-\omega_0-2\omega_Q)t}}{2}\right\}\begin{bmatrix}0&0&0&0&0&0\\-\sqrt{5}&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&\sqrt{5}&0\end{bmatrix} \\
& +\left\{\frac{e^{i(-\omega_{rf}+\omega_0+2\omega_Q)t}}{2}+\frac{e^{i(-\omega_{rf}+\omega_0-2\omega_Q)t}}{2}\right\}\begin{bmatrix}0&\sqrt{5}&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&\sqrt{5}\\0&0&0&0&0&0\end{bmatrix}+\left\{\frac{e^{i(\omega_{rf}-\omega_0+2\omega_Q)t}}{2}+\frac{e^{i(\omega_{rf}-\omega_0-2\omega_Q)t}}{2}\right\}\begin{bmatrix}0&0&0&0&0&0\\\sqrt{5}&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&\sqrt{5}&0\end{bmatrix} \\
& +\left\{\frac{e^{i(-\omega_{rf}+\omega_0+\omega_Q)t}}{2}-\frac{e^{i(-\omega_{rf}+\omega_0-\omega_Q)t}}{2}\right\}\begin{bmatrix}0&0&0&0&0&0\\0&0&2\sqrt{2}&0&0&0\\0&0&0&0&0&0\\0&0&0&0&-2\sqrt{2}&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}+\left\{\frac{e^{i(\omega_{rf}-\omega_0+\omega_Q)t}}{2}-\frac{e^{i(\omega_{rf}-\omega_0-\omega_Q)t}}{2}\right\}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&-2\sqrt{2}&0&0&0&0\\0&0&0&0&0&0\\0&0&0&2\sqrt{2}&0&0\\0&0&0&0&0&0\end{bmatrix} \\
& +\left\{\frac{e^{i(-\omega_{rf}+\omega_0+\omega_Q)t}}{2}+\frac{e^{i(-\omega_{rf}+\omega_0-\omega_Q)t}}{2}\right\}\begin{bmatrix}0&0&0&0&0&0\\0&0&2\sqrt{2}&0&0&0\\0&0&0&0&0&0\\0&0&0&0&2\sqrt{2}&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}+\left\{\frac{e^{i(\omega_{rf}-\omega_0+\omega_Q)t}}{2}+\frac{e^{i(\omega_{rf}-\omega_0-\omega_Q)t}}{2}\right\}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&2\sqrt{2}&0&0&0&0\\0&0&0&0&0&0\\0&0&0&2\sqrt{2}&0&0\\0&0&0&0&0&0\end{bmatrix}\Bigg\}
\end{aligned}
\tag{3.57}
$$

In the case of non-selective excitations, the above Hamiltonian reduces to a much simpler form . This result is in agreement with the earlier descriptions involving I = 1 & 3/2 systems.

$$\tilde{\tilde{H}} - \frac{\hbar\omega_1}{2}\begin{bmatrix} 0 & \sqrt{5} & 0 & 0 & 0 & 0 \\ \sqrt{5} & 0 & 2\sqrt{2} & 0 & 0 & 0 \\ 0 & 2\sqrt{2} & 0 & 3 & 0 & 0 \\ 0 & 0 & 3 & 0 & 2\sqrt{2} & 0 \\ 0 & 0 & 0 & 2\sqrt{2} & 0 & \sqrt{5} \\ 0 & 0 & 0 & 0 & \sqrt{5} & 0 \end{bmatrix} \tag{3.58}$$

The selective excitations comprise of two sets of satellite transitions and one central transition.

$$\left.\begin{array}{l} \text{Case 1} \Rightarrow \omega_{rf} = \omega_0 + \omega_Q \\ \text{Case 2} \Rightarrow \omega_{rf} = \omega_0 - \omega_Q \end{array}\right\} \rightarrow \text{ first set of satellite transition} \tag{3.59a}$$

$$\left.\begin{array}{l} \text{Case 3} \Rightarrow \omega_{rf} = \omega_0 + 2\omega_Q \\ \text{Case 4} \Rightarrow \omega_{rf} = \omega_0 - 2\omega_Q \end{array}\right\} \rightarrow \text{ second set of satellite transition} \tag{3.59b}$$

$$\text{Case 5} \Rightarrow \omega_{rf} = \omega_0 \} \rightarrow \text{ central transition} \tag{3.59c}$$

The effective RF Hamiltonians corresponding to these transitions are represented below by eqns. (3.60), (3.61), (3.62), (3.63), (3.64) respectively.

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2\sqrt{2} & 0 & 0 & 0 \\ 0 & 2\sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \tag{3.60}$$

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2\sqrt{2} & 0 \\ 0 & 0 & 0 & 2\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \tag{3.61}$$

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\begin{bmatrix} 0 & \sqrt{5} & 0 & 0 & 0 & 0 \\ \sqrt{5} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \tag{3.62}$$

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \sqrt{5} \\ 0 & 0 & 0 & 0 & \sqrt{5} & 0 \end{bmatrix} \tag{3.63}$$

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 3 & 0 & 0 \\ 0 & 0 & 3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \tag{3.64}$$

The transformed density operator and the detection operator for a spin *I* = 5/2 system are depicted below by eqn. (3.65) and (3.66) respectively

$$\tilde{\tilde{\rho}}(0) = \frac{1}{2}\begin{bmatrix} 5 & 0 & 0 & 0 & 0 & 0 \\ 0 & 3 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -3 & 0 \\ 0 & 0 & 0 & 0 & 0 & 5 \end{bmatrix} \tag{3.65}$$

$$\tilde{\tilde{I}}^{+} = \left\{ \frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 3 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} + i\left\{Sin(2\omega_Q t)\right\}\begin{bmatrix} 0 & \sqrt{5} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\sqrt{5} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} + \{Cos(2\omega_Q t) - 1/2\}\begin{bmatrix} 0 & \sqrt{5} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \sqrt{5} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \right.$$

$$\left. + i\left\{Sin(\omega_Q t)\right\}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2\sqrt{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -2\sqrt{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} + \{Cos(\omega_Q t) - 1/2\}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2\sqrt{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2\sqrt{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \right\} \exp(i\omega_0 t) \tag{3.66}$$

3.2.4.4 Evolution of density matrix

A) Non-selective excitations

In the case non-selective excitation, the density operator after a single pulse is evaluated [for detail see eqn.(9) of appendix 3] and represented below,

$$\rho(t)=Cos\left(\omega_1 t\right)\frac{1}{2}\begin{bmatrix}5&0&0&0&0&0\\0&3&0&0&0&0\\0&0&1&0&0&0\\0&0&0&-1&0&0\\0&0&0&0&-3&0\\0&0&0&0&0&5\end{bmatrix}-iSin\left(\omega_1 t\right)\frac{1}{2}\begin{bmatrix}0&-\sqrt{5}&0&0&0&0\\\sqrt{5}&0&-2\sqrt{2}&0&0&0\\0&2\sqrt{2}&0&-3&0&0\\0&0&3&0&-2\sqrt{2}&0\\0&0&0&2\sqrt{2}&0&-\sqrt{5}\\0&0&0&0&\sqrt{5}&0\end{bmatrix} \quad (3.67)$$

Employing the trace expression, the time domain signal is evaluated [see eqn. (10) of appendix 3] and given below,

$$\left\langle \tilde{\tilde{I}}^{+}\right\rangle = N^2 Sin\left(\omega_1 t\right)\left\{\frac{9}{2}e^{i\omega_0 t}+5\frac{e^{i2\omega_Q t+i\omega_0 t}+e^{-i2\omega_Q t+i\omega_0 t}}{2}+8\frac{e^{i\omega_Q t+i\omega_0 t}+e^{-i\omega_Q t+i\omega_0 t}}{2}\right\} \quad (3.68)$$

From eqn. (3.86), the maximum intensity obtained for time domain signal in non-selective excitation is N^2, when $Sin\left(\omega_1 t\right)$ is equal to unity, i.e. $t=\frac{\pi}{2\omega_1}$

B) Selective excitations

In the cases of selective excitations, we have a central transition and two sets of satellite transitions

1) Central transition ($\omega_{rf}=\omega_0$)

The density operator and the time domain signal [for detail see eqn. (19) and (20) of appendix 3] is represented by eqns. (3.69) and (3.70) below,

$$\rho(t)=\frac{1}{2}\begin{bmatrix}5&0&0&0&0&0\\0&3&0&0&0&0\\0&0&1&0&0&0\\0&0&0&-1&0&0\\0&0&0&0&-3&0\\0&0&0&0&0&5\end{bmatrix}-iSin\left(3\omega_1 t\right)\frac{1}{2}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&-1&0&0\\0&0&1&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}+\left\{Cos\left(3\omega_1 t\right)-1\right\}\frac{1}{2}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&1&0&0&0\\0&0&0&-1&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix} \quad (3.69)$$

$$\left\langle \tilde{\tilde{I}}^{+} \right\rangle = \frac{3}{2} N^2 Sin\left(3\omega_1 t\right) \exp(i\omega_0 t) \tag{3.70}$$

From eqn. (3.70), the maximum intensity obtained for time domain signal in the case of central transition is $\frac{3}{2}N^2$, when $Sin\left(3\omega_1 t\right)$ is equal to unity, i.e. $t = \frac{\pi}{6\omega_1}$

2) Satellite transitions

First set of satellite transitions: $(\omega_{rf} = \omega_0 \pm \omega_Q)$,

When $\omega_{rf} = \omega_0 + \omega_Q$, the evolved density operator and the time domain signals [see eqn. (11) and (12) of appendix 3] is represented by,

$$\rho(t) = \frac{1}{2}\begin{bmatrix} 5 & 0 & 0 & 0 & 0 & 0 \\ 0 & 3 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -3 & 0 \\ 0 & 0 & 0 & 0 & 0 & 5 \end{bmatrix} - iSin\left(2\sqrt{2}\omega_1 t\right)\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} + \left\{Cos\left(2\sqrt{2}\omega_1 t\right) - 1\right\}\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \tag{3.71}$$

$$\left\langle \tilde{\tilde{I}}^{+} \right\rangle = \sqrt{2} N^2 iSin\left(2\sqrt{2}\omega_1 t\right) e^{i\omega_Q t + i\omega_0 t} \tag{3.72}$$

In similar vein, time domain signal for matching condition $(\omega_{rf} = \omega_0 - \omega_Q)$, is represented by,

$$\left\langle \tilde{\tilde{I}}^{+} \right\rangle = \sqrt{2} N^2 iSin\left(2\sqrt{2}\omega_1 t\right) e^{-i\omega_Q t + i\omega_0 t} \tag{3.73}$$

From eqns. (3.72) and (3.73), the maximum intensity obtained for time domain signal in this satellite transition is $\sqrt{2}N^2$, when $Sin\left(2\sqrt{2}\omega_1 t\right)$ is equal to unity, i.e. $t = \frac{\pi}{4\sqrt{2}\omega_1}$

Second set of satellite transitions: $\omega_{rf} = \left(\omega_0 \pm 2\omega_Q\right)$

In the case of $\omega_{rf} = \left(\omega_0 + 2\omega_Q\right)$, the evolved density operator and the time domain signal [see eqn. (15) and (16) of appendix 3] is represented by,

$$\rho(t)=\frac{1}{2}\begin{bmatrix}5&0&0&0&0&0\\0&3&0&0&0&0\\0&0&1&0&0&0\\0&0&0&-1&0&0\\0&0&0&0&-3&0\\0&0&0&0&0&5\end{bmatrix}-iSin\left(\sqrt{5}\omega_1 t\right)\frac{1}{2}\begin{bmatrix}0&-1&0&0&0&0\\1&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}+\left\{Cos\left(\sqrt{5}\omega_1 t\right)-1\right\}\frac{1}{2}\begin{bmatrix}1&0&0&0&0&0\\0&-1&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix} \tag{3.74}$$

$$\left\langle \tilde{\tilde{I}}^{+}\right\rangle=\frac{\sqrt{5}}{2}N^2 Sin\left(\sqrt{5}\omega_1 t\right)e^{i2\omega_Q t+i\omega_0 t} \tag{3.75}$$

From eqn. (3.36), the maximum intensity obtained for time domain signal

In a similar vein, when $\omega_{rf}=\left(\omega_0-2\omega_Q\right)$, the time domain signal is represented by,

$$\left\langle \tilde{\tilde{I}}^{+}\right\rangle=\frac{\sqrt{5}}{2}N^2 Sin\left(\sqrt{5}\omega_1 t\right)e^{-i2\omega_Q t+i\omega_0 t} \tag{3.76}$$

From eqns. (3.75) and (3.76), the maximum intensity obtained for time domain signal in this set of satellite transition is $\frac{\sqrt{5}}{2}N^2$, when $Sin\left(\sqrt{5}\omega_1 t\right)$ is equal to unity, i.e. $t=\frac{\pi}{2\sqrt{5}\omega_1}$

The summary of our calculations for spin I =5/2 are tabulated below in table 4.

Table 3. Summary of spin *I* = 5/2 results.

S.No.	Matching Condition	Frequency	Intensity	Pulse duration
1	$\omega_{rf}=\omega_0+\omega_Q$	$\omega_0+\omega_Q$	$\sqrt{2}N^2$	$\frac{\pi}{4\sqrt{2}\omega_1}$
2	$\omega_{rf}=\omega_0-\omega_Q$	$\omega_0-\omega_Q$	$\sqrt{2}N^2$	$\frac{\pi}{4\sqrt{2}\omega_1}$
3	$\omega_{rf}=\omega_0+2\omega_Q$	$\omega_0+2\omega_Q$	$\frac{\sqrt{5}}{2}N^2$	$\frac{\pi}{2\sqrt{5}\omega_1}$
4	$\omega_{rf}=\omega_0-2\omega_Q$	$\omega_0-2\omega_Q$	$\frac{\sqrt{5}}{2}N^2$	$\frac{\pi}{2\sqrt{5}\omega_1}$
5	$\omega_{rf}=\omega_0$	ω_0	$\frac{3}{2}N^2$	$\frac{\pi}{6\omega_1}$
6	Hard pulse	All five frequencies	$\frac{9}{2}N^2,\frac{5}{2}N^2,\frac{5}{2}N^2,$ $4N^2,4N^2$	$\frac{\pi}{2\omega_1}$

In table 3, value of N is $\sqrt{\frac{2}{35}}$.

Below, we are presenting the numerically simulated spectrum of spin I = 5/2, for varying symmetries (η = 0, 0.5, 1). In agreement with our formalism spin I = 5/2 spectrum, depicts a central band and two set of satellite transitions.

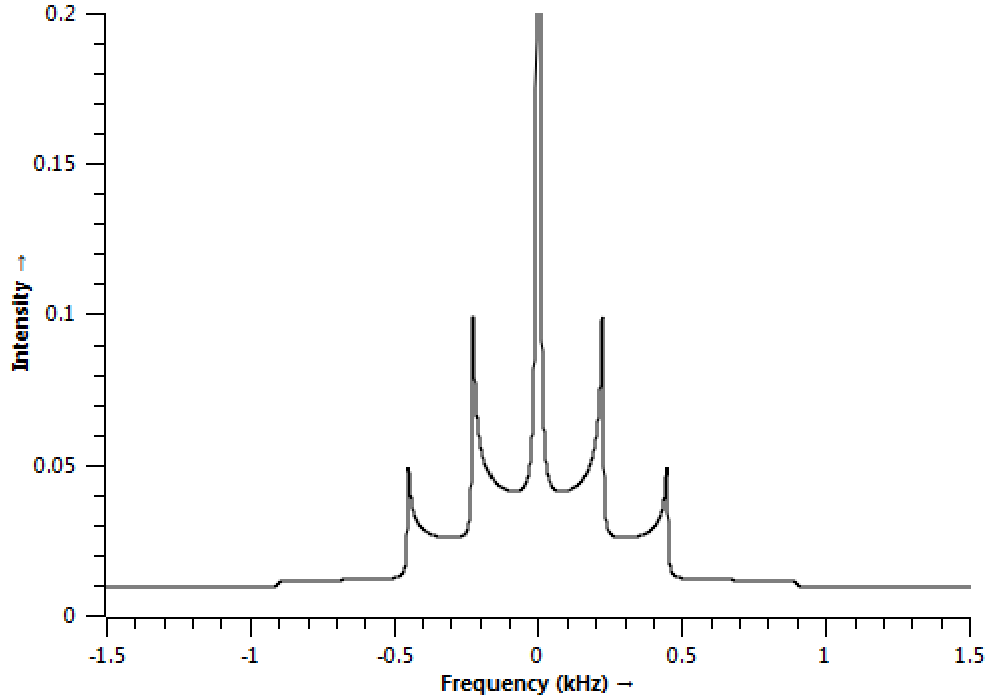

FIGURE 11(A). POWDER AVERAGED SPECTRUM OF SPIN I = 5/2, WITH η=0.

This is a hard pulse (π/2) spectrum for ^{27}Al nuclei (spin I = 5/2) acquired over 6044 orientations, with quadrupolar constant, ω_Q = 6/35 KHz, and C_Q = 1 KHz.

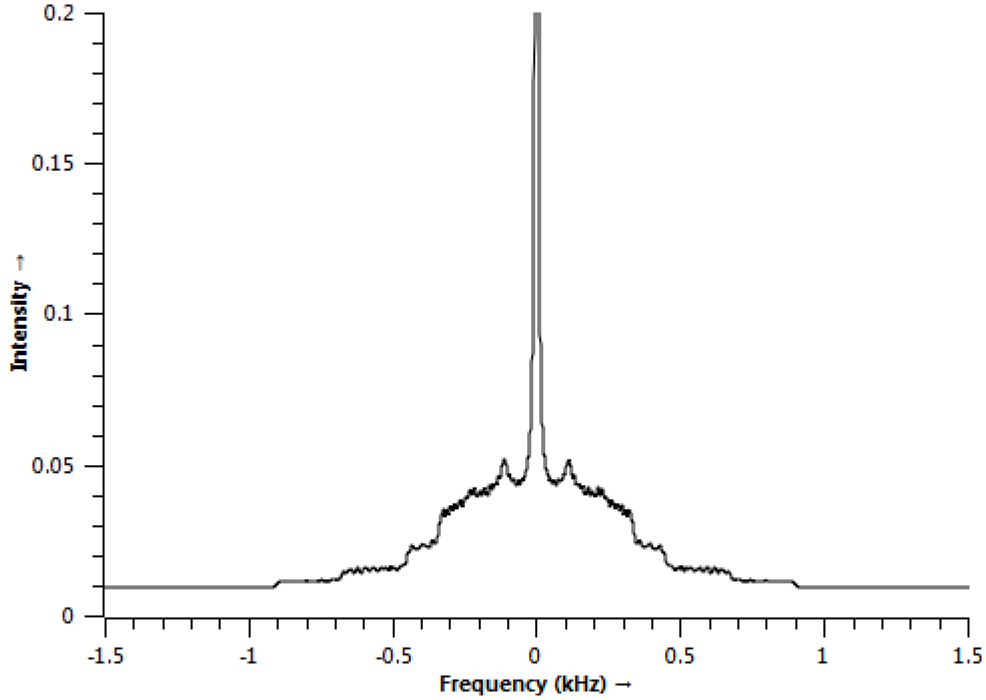

FIGURE 11(B). POWDER AVERAGED SPECTRUM OF SPIN I = 5/2, WITH η=0.5.

This is a hard pulse (π/2) spectrum for ^{27}Al nuclei (spin I = 5/2) acquired over 6044 orientations, with quadrupolar constant, ω_Q = 6/35 KHz, and C_Q = 1 KHz.

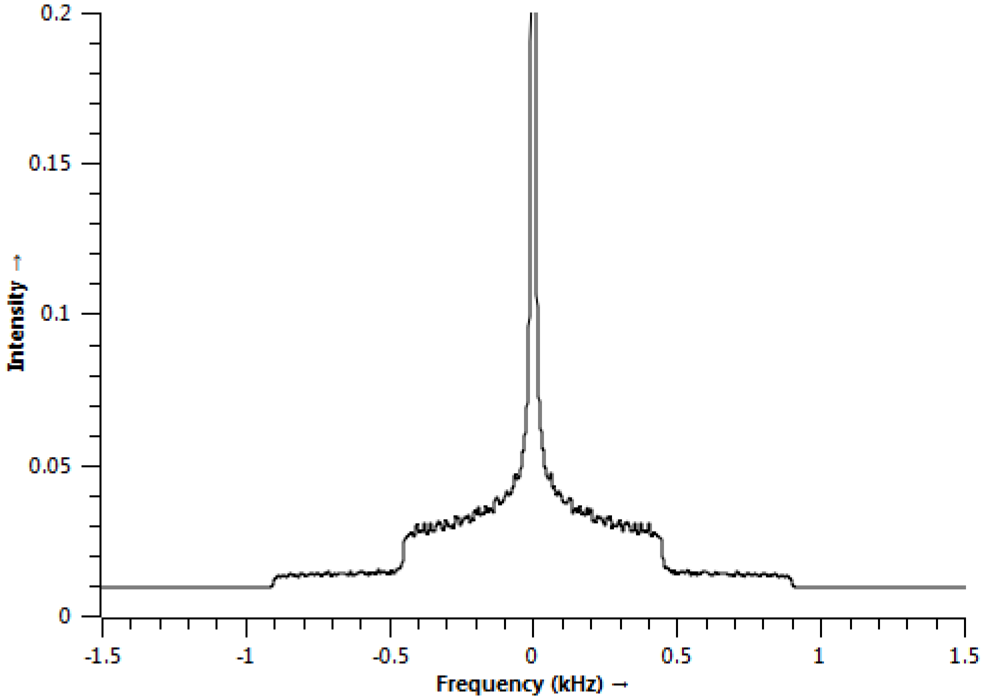

FIGURE 11(C). POWDER AVERAGED SPECTRUM OF SPIN I = 5/2, WITH η=1.0.
This is a hard pulse (π/2) spectrum for ^{27}Al nuclei (spin I = 5/2) acquired over 6044 orientations, with quadrupolar constant, ω_Q = 6/35 KHz, and C_Q = 1 KHz.

Chapter 4

Summary and Future perspectives

The effective RF Hamiltonians derived in the previous chapter presents a framework for improving the excitation efficiency in both integer and half-integer spins. In contrast to non-selective excitation, the excitation efficiency in the case of selective transitions depends on the spin states involved. For a selective transition between the levels say (for, I^{+} detection operator)

$$\left|I, M\right\rangle \rightarrow \left|I, M-1\right\rangle$$

the optimum flip angle for a spin '*I*' could be summarized by a simple relation,

$\theta = \dfrac{\pi}{2\sqrt{(I+M)(I-M+1)}}$, where M is the projection of the spin angular momentum along the z-direction. The analytic derivations presented could facilitate in improving the excitation efficiency of multi-quantum transitions employed in multi-pulse experiments and would be described elsewhere. Additionally, employing the methodology presented, we plan to investigate the effect of second order quadrupolar interactions on the spin dynamics.

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Appendices

Appendix-1

Detailed matrix algebra relating to spin *I* = 1.

1. Effective Hamiltonian

Quadrupolar interaction frame transformation:

$$\tilde{H} = I_X + \left[(3I_Z^2 - I^2), I_X\right](i\phi t) + \left[(3I_Z^2 - I^2),\left[(3I_Z^2 - I^2), I_X\right]\right]\frac{(i\phi t)^2}{2!} + \left[(3I_Z^2 - I^2),\left[(3I_Z^2 - I^2),\left[(3I_Z^2 - I^2)I_X\right]\right]\right]\frac{(i\phi t)^3}{3!} + ... \quad (1)$$

Employing, above mentioned BCH expansion, Hamiltonian in matrix representation is written as:

$$\tilde{H} = \begin{bmatrix} 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & \sqrt{2} \\ 0 & \sqrt{2} & 0 \end{bmatrix} + (i\phi t)\begin{bmatrix} 0 & 3\sqrt{2} & 0 \\ -3\sqrt{2} & 0 & -3\sqrt{2} \\ 0 & 3\sqrt{2} & 0 \end{bmatrix} + \frac{(i\phi t)^2}{2!}\begin{bmatrix} 0 & 9\sqrt{2} & 0 \\ 9\sqrt{2} & 0 & 9\sqrt{2} \\ 0 & 9\sqrt{2} & 0 \end{bmatrix} + \frac{(i\phi t)^3}{3!}3^2\begin{bmatrix} 0 & 3\sqrt{2} & 0 \\ -3\sqrt{2} & 0 & -3\sqrt{2} \\ 0 & 3\sqrt{2} & 0 \end{bmatrix} + \frac{(i\phi t)^4}{4!}3^2\begin{bmatrix} 0 & 9\sqrt{2} & 0 \\ 9\sqrt{2} & 0 & 9\sqrt{2} \\ 0 & 9\sqrt{2} & 0 \end{bmatrix}...... \quad (2)$$

Eqn.(2) is rearranged as:

$$\tilde{H} = \begin{bmatrix} 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & \sqrt{2} \\ 0 & \sqrt{2} & 0 \end{bmatrix} + \left\{(i\phi t) + \frac{(i\phi t)^3}{3!}3^2 + ...\right\}\begin{bmatrix} 0 & 3\sqrt{2} & 0 \\ -3\sqrt{2} & 0 & -3\sqrt{2} \\ 0 & 3\sqrt{2} & 0 \end{bmatrix} + \left\{\frac{(i\phi t)^2}{2!} + \frac{(i\phi t)^4}{4!}3^2........\right\}\begin{bmatrix} 0 & 9\sqrt{2} & 0 \\ 9\sqrt{2} & 0 & 9\sqrt{2} \\ 0 & 9\sqrt{2} & 0 \end{bmatrix} \quad (3)$$

Using exponential expansion of trigonometric function *Cosine* and *Sine*, eqn. (3) is written as:

$$\tilde{H} = \frac{i}{3}Sin(3\phi t)\begin{bmatrix} 0 & 3\sqrt{2} & 0 \\ -3\sqrt{2} & 0 & -3\sqrt{2} \\ 0 & 3\sqrt{2} & 0 \end{bmatrix} + \frac{1}{9}Cos(3\phi t)\begin{bmatrix} 0 & 9\sqrt{2} & 0 \\ 9\sqrt{2} & 0 & 9\sqrt{2} \\ 0 & 9\sqrt{2} & 0 \end{bmatrix} \quad (4)$$

Zeeman interaction frame transformation: Hamiltonian in Zeeman interaction frame is given by,

$$\tilde{\tilde{H}} = \exp(-i\omega_0 t I_Z)\left\{ iSin\left(\frac{\omega_Q}{2}t\right)\underbrace{\begin{bmatrix} 0 & \sqrt{2} & 0 \\ -\sqrt{2} & 0 & -\sqrt{2} \\ 0 & \sqrt{2} & 0 \end{bmatrix}}_{A} + Cos\left(\frac{\omega_Q}{2}t\right)\underbrace{\begin{bmatrix} 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & \sqrt{2} \\ 0 & \sqrt{2} & 0 \end{bmatrix}}_{B} \right\}\exp(i\omega_0 t I_Z)\left\{-\hbar\omega_1 \cos(\omega_{rf} t)\right\} \tag{5}$$

Solution for above expression (eqn. 5) is obtained by employing BCH expansion mentioned below:

$$\tilde{\tilde{H}} = X + [Y, X](i\omega_0 t) + [Y,[Y,X]]\frac{(i\omega_0 t)^2}{2!} + [Y,[Y,[Y,X]]]\frac{(i\omega_0 t)^3}{3!} + \dots\dots\dots \tag{6}$$

Action of I_Z operator on matrix A of eqn. (5) is given as:

$$\begin{bmatrix} 0 & \sqrt{2} & 0 \\ -\sqrt{2} & 0 & -\sqrt{2} \\ 0 & \sqrt{2} & 0 \end{bmatrix} + (i\omega_0 t)\begin{bmatrix} 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & -\sqrt{2} \\ 0 & -\sqrt{2} & 0 \end{bmatrix} + \frac{(i\omega_0 t)^2}{2!}\begin{bmatrix} 0 & \sqrt{2} & 0 \\ -\sqrt{2} & 0 & -\sqrt{2} \\ 0 & \sqrt{2} & 0 \end{bmatrix} + \frac{(i\omega_0 t)^3}{3!}\begin{bmatrix} 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & -\sqrt{2} \\ 0 & -\sqrt{2} & 0 \end{bmatrix} + \dots\dots\dots$$

In this expression lower diagonals are changing the signs alternatively. So after splitting in two matrices, closed form solution is given as:

$$\begin{bmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & -\sqrt{2} \\ 0 & 0 & 0 \end{bmatrix}\exp(i\omega_0 t) + \begin{bmatrix} 0 & 0 & 0 \\ -\sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{bmatrix}\exp(-i\omega_0 t) \tag{7a}$$

Similarly, action of I_Z on matrix B of eqn. (5) is given as:

$$\begin{bmatrix} 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & \sqrt{2} \\ 0 & \sqrt{2} & 0 \end{bmatrix} + (i\omega_0 t)\begin{bmatrix} 0 & \sqrt{2} & 0 \\ -\sqrt{2} & 0 & \sqrt{2} \\ 0 & -\sqrt{2} & 0 \end{bmatrix} + \frac{(i\omega_0 t)^2}{2!}\begin{bmatrix} 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & \sqrt{2} \\ 0 & \sqrt{2} & 0 \end{bmatrix} + \frac{(i\omega_0 t)^3}{3!}\begin{bmatrix} 0 & \sqrt{2} & 0 \\ -\sqrt{2} & 0 & \sqrt{2} \\ 0 & -\sqrt{2} & 0 \end{bmatrix} + \dots\dots$$

Here, also lower diagonal changes the sign alternatively. Hence after splitting matrices solution is given as:

$$\begin{bmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{bmatrix}\exp(i\omega_0 t) + \begin{bmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{bmatrix}\exp(-i\omega_0 t) \tag{7b}$$

Using results of eqn. (7), solution of eqn. (5) is written as:

$$\tilde{\tilde{H}} = \left\{ \begin{array}{l} iSin\left(\frac{\omega_Q}{2}t\right)\left(\begin{bmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & -\sqrt{2} \\ 0 & 0 & 0 \end{bmatrix}\exp(i\omega_0 t) + \begin{bmatrix} 0 & 0 & 0 \\ -\sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{bmatrix}\exp(-i\omega_0 t)\right) \\ +Cos\left(\frac{\omega_Q}{2}t\right)\left(\begin{bmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{bmatrix}\exp(i\omega_0 t) + \begin{bmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{bmatrix}\exp(-i\omega_0 t)\right) \end{array} \right\} \left\{-\hbar\omega_1 \cos(\omega_{rf} t)\right\} \tag{8}$$

2. Evolution of density matrix

Evolved density matrix under effective Hamiltonian is obtained by:

$$\rho(t) = \rho(0) + \left(\frac{i}{\hbar}t\right)\left[H, \rho(0)\right] + \frac{1}{2!}\left(\frac{i}{\hbar}t\right)^2 \left[H, \left[H, \rho(0)\right]\right] + ...$$

The initial density matrix for spin-1 nuclei is given by:

$$\tilde{\tilde{\rho}}(0) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

A) Hard pulse regime: Hamiltonian [see eqn. (3.27)] is represented by,

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\begin{bmatrix} 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & \sqrt{2} \\ 0 & \sqrt{2} & 0 \end{bmatrix}$$

Density matrix evolved under this Hamiltonian, is given by:

$$\rho(t) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} + (-i\omega_1 t)\frac{1}{2}\begin{bmatrix} 0 & -\sqrt{2} & 0 \\ \sqrt{2} & 0 & -\sqrt{2} \\ 0 & \sqrt{2} & 0 \end{bmatrix} + \frac{(-i\omega_1 t)^2}{2!}\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} + \frac{(-i\omega_1 t)^3}{3!}\frac{1}{2}\begin{bmatrix} 0 & -\sqrt{2} & 0 \\ \sqrt{2} & 0 & -\sqrt{2} \\ 0 & \sqrt{2} & 0 \end{bmatrix}$$

$$+ \frac{(-i\omega_1 t)^4}{4!}\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} + \frac{(-i\omega_1 t)^5}{5!}\frac{1}{2}\begin{bmatrix} 0 & -\sqrt{2} & 0 \\ \sqrt{2} & 0 & -\sqrt{2} \\ 0 & \sqrt{2} & 0 \end{bmatrix} + \frac{(-i\omega_1 t)^6}{6!}\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} .....$$

$$\Rightarrow \rho(t) = \left\{ (-i\omega_1 t) + \frac{(-i\omega_1 t)^3}{3!} + \frac{(-i\omega_1 t)^5}{5!} + \frac{(-i\omega_1 t)^7}{7!} \ldots\ldots \right\} \frac{1}{2} \begin{bmatrix} 0 & -\sqrt{2} & 0 \\ \sqrt{2} & 0 & -\sqrt{2} \\ 0 & \sqrt{2} & 0 \end{bmatrix}$$

$$+ \left\{ 1 + \frac{(-i\omega_1 t)^2}{2!} + \frac{(-i\omega_1 t)^4}{4!} + \frac{(-i\omega_1 t)^6}{6!} + \ldots\ldots \right\} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$\Rightarrow \rho(t) = Cos(\omega_1 t) \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} - iSin(\omega_1 t) \frac{1}{2} \begin{bmatrix} 0 & -\sqrt{2} & 0 \\ \sqrt{2} & 0 & -\sqrt{2} \\ 0 & \sqrt{2} & 0 \end{bmatrix} \quad (9)$$

Expectation value of time domain signal is given by:

$$\left\langle \tilde{\tilde{I}}^{+} \right\rangle = Tr\left[\rho(t).\tilde{\tilde{I}}^{+} \right]$$

$$\left\langle \tilde{\tilde{I}}^{+} \right\rangle = Tr\left[-iSin(\omega_1 t) \frac{1}{2} \left\{ iSin\left[\frac{\omega_Q}{2} t \right] \begin{bmatrix} 0 & 0 & 2 \\ 0 & 2 & 0 \\ 0 & 0 & -2 \end{bmatrix} \exp(i\omega_0 t) + Cos\left[\frac{\omega_Q}{2} t \right] \begin{bmatrix} 0 & 0 & -2 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{bmatrix} \exp(i\omega_0 t) \right\} \right]$$

$$\Rightarrow \left\langle \tilde{\tilde{I}}^{+} \right\rangle = -2iSin(\omega_1 t) \left\{ Cos\left[\frac{\omega_Q}{2} t \right] \exp(i\omega_0 t) \right\} \quad (10)$$

Maximum intensity is N^2, when $Sin(\omega_1 t)$ is equal to unity, i.e. $t = \frac{\pi}{2\omega_1}$

B) Soft Pulse regime

Case 1: Effective Hamiltonian [see eqn. (3.29)] is represented as:

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & \sqrt{2} & 0 \end{bmatrix}$$

Density matrix evolved under this Hamiltonian, is given by:

$$\rho(t) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} + (-i\omega_1 t) \frac{1}{2} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -\sqrt{2} \\ 0 & \sqrt{2} & 0 \end{bmatrix} + \frac{(-i\omega_1 t)^2}{2!} \frac{1}{2} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & -2 \end{bmatrix} + \frac{(-i\omega_1 t)^3}{3!} \frac{1}{2} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -2\sqrt{2} \\ 0 & 2\sqrt{2} & 0 \end{bmatrix}$$

$$+ \frac{(-i\omega_1 t)^4}{4!} \frac{1}{2} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 4 & 0 \\ 0 & 0 & -4 \end{bmatrix} + \frac{(-i\omega_1 t)^5}{5!} \frac{1}{2} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -4\sqrt{2} \\ 0 & 4\sqrt{2} & 0 \end{bmatrix} + \frac{(-i\omega_1 t)^6}{6!} \frac{1}{2} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 8 & 0 \\ 0 & 0 & -8 \end{bmatrix} \ldots\ldots$$

$$\Rightarrow \rho(t) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} + \left\{ \left(-\sqrt{2} i\omega_1 t\right) + \frac{\left(-\sqrt{2} i\omega_1 t\right)^3}{3!} + \frac{\left(-\sqrt{2} i\omega_1 t\right)^5}{5!} + \frac{\left(-\sqrt{2} i\omega_1 t\right)^7}{7!} .... \right\} \frac{1}{2} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix}$$

$$+ \left\{ \frac{\left(-\sqrt{2} i\omega_1 t\right)^2}{2!} + \frac{\left(-\sqrt{2} i\omega_1 t\right)^4}{4!} + \frac{\left(-\sqrt{2} i\omega_1 t\right)^6}{6!} + ... \right\} \frac{1}{2} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$\Rightarrow \rho(t) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} - iSin\left(\sqrt{2}\omega_1 t\right) \frac{1}{2} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix} + \left\{ Cos\left(\sqrt{2}\omega_1 t\right) - 1 \right\} \frac{1}{2} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \tag{11}$$

$$\left\langle \tilde{\tilde{I}}^{+} \right\rangle = Tr \left[-iSin\left(\sqrt{2}\omega_1 t\right) \frac{1}{2} \left\{ iSin\left[\frac{\omega_Q}{2} t\right] \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -\sqrt{2} \end{bmatrix} \exp(i\omega_0 t) + Cos\left[\frac{\omega_Q}{2} t\right] \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \sqrt{2} \end{bmatrix} \exp(i\omega_0 t) \right\} \right]$$

$$\Rightarrow \left\langle \tilde{\tilde{I}}^{+} \right\rangle = -\frac{1}{\sqrt{2}} iSin\left(\sqrt{2}\omega_1 t\right) \left\{ -iSin\left[\frac{\omega_Q}{2} t\right] \exp(i\omega_0 t) + Cos\left[\frac{\omega_Q}{2} t\right] \exp(i\omega_0 t) \right\} \tag{12}$$

Maximum intensity is $\frac{1}{\sqrt{2}} N^2$, when $Sin\left(\sqrt{2}\omega_1 t\right)$ is equal to unity, i.e. $t = \frac{\pi}{2\sqrt{2}\omega_1}$

Case 2: Effective Hamiltonian [see eqn. (3.30)] for this matching condition is represented as:

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2} \begin{bmatrix} 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Density matrix evolved under this Hamiltonian, is given by:

$$\rho(t) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} + \left(-i\omega_1 t\right) \frac{1}{2} \begin{bmatrix} 0 & -\sqrt{2} & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \frac{\left(-i\omega_1 t\right)^2}{2!} \frac{1}{2} \begin{bmatrix} 2 & 0 & 0 \\ 0 & -2 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \frac{\left(-i\omega_1 t\right)^3}{3!} \frac{1}{2} \begin{bmatrix} 0 & -2\sqrt{2} & 0 \\ 2\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$+ \frac{\left(-i\omega_1 t\right)^4}{4!} \frac{1}{2} \begin{bmatrix} 4 & 0 & 0 \\ 0 & -4 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \frac{\left(-i\omega_1 t\right)^5}{5!} \frac{1}{2} \begin{bmatrix} 0 & -4\sqrt{2} & 0 \\ 4\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \frac{\left(-i\omega_1 t\right)^6}{6!} \frac{1}{2} \begin{bmatrix} 8 & 0 & 0 \\ 0 & -8 & 0 \\ 0 & 0 & 0 \end{bmatrix} .....$$

$$\Rightarrow \rho(t)=\begin{bmatrix}1&0&0\\0&0&0\\0&0&-1\end{bmatrix}+\left\{\left(-\sqrt{2}i\omega_1 t\right)+\frac{\left(-\sqrt{2}i\omega_1 t\right)^3}{3!}+\frac{\left(-\sqrt{2}i\omega_1 t\right)^5}{5!}+\frac{\left(-\sqrt{2}i\omega_1 t\right)^7}{7!}.......\right\}\frac{1}{2}\begin{bmatrix}0&-1&0\\1&0&0\\0&0&0\end{bmatrix}$$

$$+\left\{\frac{\left(-\sqrt{2}i\omega_1 t\right)^2}{2!}+\frac{\left(-\sqrt{2}i\omega_1 t\right)^4}{4!}+\frac{\left(-\sqrt{2}i\omega_1 t\right)^6}{6!}+.....\right\}\frac{1}{2}\begin{bmatrix}1&0&0\\0&-1&0\\0&0&0\end{bmatrix}$$

$$\Rightarrow \rho(t)=\begin{bmatrix}1&0&0\\0&0&0\\0&0&-1\end{bmatrix}-iSin\left(\sqrt{2}\omega_1 t\right)\frac{1}{2}\begin{bmatrix}0&-1&0\\1&0&0\\0&0&0\end{bmatrix}+\left\{Cos\left(\sqrt{2}\omega_1 t\right)-1\right\}\frac{1}{2}\begin{bmatrix}1&0&0\\0&-1&0\\0&0&0\end{bmatrix} \qquad (13)$$

$$\left\langle .\tilde{\tilde{I}}_+\right\rangle = Tr\left[-iSin\left(\sqrt{2}\omega_1 t\right)\frac{1}{2}\left\{iSin\left[\frac{\omega_Q}{2}t\right]\begin{bmatrix}0&0&0\\0&0&0\\0&0&-\sqrt{2}\end{bmatrix}\exp(i\omega_0 t)+Cos\left[\frac{\omega_Q}{2}t\right]\begin{bmatrix}0&0&0\\0&0&0\\0&0&\sqrt{2}\end{bmatrix}\exp(i\omega_0 t)\right\}\right]$$

$$\Rightarrow \left\langle .\tilde{\tilde{I}}_+\right\rangle = -\frac{1}{\sqrt{2}}iSin\left(\sqrt{2}\omega_1 t\right)\left\{-iSin\left[\frac{\omega_Q}{2}t\right]\exp(i\omega_0 t)+Cos\left[\frac{\omega_Q}{2}t\right]\exp(i\omega_0 t)\right\} \qquad (14)$$

Maximum intensity is $\frac{1}{\sqrt{2}}N^2$, when $Sin\left(\sqrt{2}\omega_1 t\right)$ is equal to unity, i.e. $t=\frac{\pi}{2\sqrt{2}\omega_1}$

Appendix 2

Detailed matrix algebra for spin *I* = 3/2.

1. Effective Hamiltonian

Quadrupolar interaction frame transformation:

$$\tilde{H} = I_X + \left[(3I_Z^2 - I^2), I_X\right](i\phi t) + \left[(3I_Z^2 - I^2),\left[(3I_Z^2 - I^2), I_X\right]\right]\frac{(i\phi t)^2}{2!} + \left[(3I_Z^2 - I^2),\left[(3I_Z^2 - I^2),\left[(3I_Z^2 - I^2)I_X\right]\right]\right]\frac{(i\phi t)^3}{3!} + ... \tag{1}$$

Employing, above mentioned BCH expansion, Hamiltonian in matrix representation is written as:

$$\tilde{H} = \frac{1}{2}\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix} + (i\phi t).6.\frac{1}{2}\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix} + \frac{(i\phi t)^2}{2!}.6^2.\frac{1}{2}\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix}$$
$$+ \frac{(i\phi t)^3}{3!}6^{.3}.\frac{1}{2}\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix} + \frac{(i\phi t)^4}{4!}6^4.\frac{1}{2}\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix} + ... \tag{2}$$

Above expression, eqn. (2) is rearranged as:

$$\tilde{H} = \frac{1}{2}\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix} + \left\{(i6\phi t) + \frac{(i6\phi t)^3}{3!} + ...\right\}.\frac{1}{2}.\frac{1}{6}\begin{bmatrix} 0 & 6\sqrt{3} & 0 & 0 \\ -6\sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & -6\sqrt{3} \\ 0 & 0 & 6\sqrt{3} & 0 \end{bmatrix}$$
$$+ \left\{\frac{(i\phi t)^2}{2!} + \frac{(i\phi t)^4}{4!}3^2........\right\}\frac{1}{2}.\frac{1}{36}\begin{bmatrix} 0 & 36\sqrt{3} & 0 & 0 \\ 36\sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 36\sqrt{3} \\ 0 & 0 & 36\sqrt{3} & 0 \end{bmatrix} \tag{3}$$

Using exponential expansion of trigonometric functions *Cosine* and *Sine*, eqn. (3) is written as:

$$\tilde{H}=\frac{1}{2}\begin{bmatrix}0&\sqrt{3}&0&0\\ \sqrt{3}&0&2&0\\ 0&2&0&\sqrt{3}\\ 0&0&\sqrt{3}&0\end{bmatrix}+\frac{i}{2}Sin(6\phi t)\begin{bmatrix}0&\sqrt{3}&0&0\\ -\sqrt{3}&0&0&0\\ 0&0&0&-\sqrt{3}\\ 0&0&\sqrt{3}&0\end{bmatrix}+\frac{1}{2}\{Cos(6\phi t)-1\}\begin{bmatrix}0&\sqrt{3}&0&0\\ \sqrt{3}&0&0&0\\ 0&0&0&\sqrt{3}\\ 0&0&\sqrt{3}&0\end{bmatrix} \tag{4}$$

Zeeman interaction frame transformation: Hamiltonian in Zeeman interaction frame is given by:

$$\tilde{\tilde{H}}=\exp(-i\omega_0 tI_Z)\left\{\underbrace{\begin{bmatrix}0&0&0&0\\0&0&2&0\\0&2&0&0\\0&0&0&0\end{bmatrix}}_{A}+iSin(\omega_Q t)\underbrace{\begin{bmatrix}0&\sqrt{3}&0&0\\ -\sqrt{3}&0&0&0\\ 0&0&0&-\sqrt{3}\\ 0&0&\sqrt{3}&0\end{bmatrix}}_{B}+Cos(\omega_Q t)\underbrace{\begin{bmatrix}0&\sqrt{3}&0&0\\ \sqrt{3}&0&0&0\\ 0&0&0&\sqrt{3}\\ 0&0&\sqrt{3}&0\end{bmatrix}}_{C}\right\}\exp(i\omega_0 tI_Z)$$
$$\times\left\{-\hbar\omega_1\cos(\omega_{rf}t)\right\} \tag{5}$$

Solution for above expression is obtained by employing BCH expansion mentioned below:

$$\tilde{\tilde{H}}=X+[Y,X](i\omega_0 t)+\left[Y,[Y,X]\right]\frac{(i\omega_0 t)^2}{2!}+\left[Y,\left[Y,[Y,X]\right]\right]\frac{(i\omega_0 t)^3}{3!}+\ldots\ldots\ldots \tag{6}$$

Action of I_Z operator on matrix A of eqn. (5) is given as:

$$\begin{bmatrix}0&0&0&0\\0&0&2&0\\0&2&0&0\\0&0&0&0\end{bmatrix}+(i\omega_0 t)\begin{bmatrix}0&0&0&0\\0&0&2&0\\0&-2&0&0\\0&0&0&0\end{bmatrix}+\frac{(i\omega_0 t)^2}{2!}\begin{bmatrix}0&0&0&0\\0&0&2&0\\0&2&0&0\\0&0&0&0\end{bmatrix}+\frac{(i\omega_0 t)^3}{3!}\begin{bmatrix}0&0&0&0\\0&0&2&0\\0&-2&0&0\\0&0&0&0\end{bmatrix}+\ldots\ldots\ldots$$

In above expression lower element changes its polarity alternatively, by splitting the matrices closed solution of above expression is given as:

$$\begin{bmatrix}0&0&0&0\\0&0&2&0\\0&0&0&0\\0&0&0&0\end{bmatrix}\exp(i\omega_0 t)+\begin{bmatrix}0&0&0&0\\0&0&0&0\\0&2&0&0\\0&0&0&0\end{bmatrix}\exp(-i\omega_0 t) \tag{7a}$$

Similarly, action of I_Z on matrix B of eqn. (5) is given as:

$$\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix} + (i\omega_0 t)\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{3} \\ 0 & 0 & -\sqrt{3} & 0 \end{bmatrix} + \frac{(i\omega_0 t)^2}{2!}\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix}$$

$$+\frac{(i\omega_0 t)^3}{3!}\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{3} \\ 0 & 0 & -\sqrt{3} & 0 \end{bmatrix} + \frac{(i\omega_0 t)^4}{4!}\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{3} \\ 0 & 0 & -\sqrt{3} & 0 \end{bmatrix} + \frac{(i\omega_0 t)^5}{5!}\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix} \ldots\ldots\ldots$$

Here, also lower diagonal changes the polarity alternatively. After splitting matrices, closed form solution is given by:

$$\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{3} \\ 0 & 0 & 0 & 0 \end{bmatrix} \exp(i\omega_0 t) + \begin{bmatrix} 0 & 0 & 0 & 0 \\ -\sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix} \exp(-i\omega_0 t) \qquad (7b)$$

Similarly, action of I_Z on matrix C of eqn. (5) is given as

$$\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix} + (i\omega_0 t)\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & -\sqrt{3} & 0 \end{bmatrix} + \frac{(i\omega_0 t)^2}{2!}\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix} +$$

$$+\frac{(i\omega_0 t)^3}{3!}\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & -\sqrt{3} & 0 \end{bmatrix} + \frac{(i\omega_0 t)^4}{4!}\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix} + \frac{(i\omega_0 t)^5}{5!}\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & -\sqrt{3} & 0 \end{bmatrix} \ldots\ldots\ldots$$

Similarly, here also lower diagonal changes the polarity alternatively. After splitting matrices, closed form solution is given by:

$$\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & 0 & 0 \end{bmatrix} \exp(i\omega_0 t) + \begin{bmatrix} 0 & 0 & 0 & 0 \\ \sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix} \exp(-i\omega_0 t) \qquad (7c)$$

Using results of eqn. (7), solution of eqn. (5) is written as:

$$\tilde{\tilde{H}} = \left\{-\hbar\omega_1 \cos(\omega_{rf} t)\right\} \left\{ \left(\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \exp(i\omega_0 t) + \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \exp(-i\omega_0 t) \right) \right.$$

$$+ iSin(\omega_Q t) \left(\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{3} \\ 0 & 0 & 0 & 0 \end{bmatrix} \exp(i\omega_0 t) + \begin{bmatrix} 0 & 0 & 0 & 0 \\ -\sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix} \exp(-i\omega_0 t) \right) \quad (8)$$

$$\left. + Cos(\omega_Q t) \left(\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & 0 & 0 \end{bmatrix} \exp(i\omega_0 t) + \begin{bmatrix} 0 & 0 & 0 & 0 \\ \sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix} \exp(-i\omega_0 t) \right) \right\}$$

2. Evolution of density matrix

Evolved density matrix under effective Hamiltonian is obtained by:

$$\rho(t) = \rho(0) + \left(\frac{i}{\hbar} t\right)\left[H, \rho(0)\right] + \frac{1}{2!}\left(\frac{i}{\hbar} t\right)^2 \left[H, \left[H, \rho(0)\right]\right] + ...$$

The initial density matrix for spin-3/2 nuclei is given by:

$$\tilde{\tilde{\rho}}(0) = \frac{1}{2} \begin{bmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{bmatrix}$$

A) Hard pulse regime

Effective Hamiltonian [see eqn. (3.43)] is represented as:

$$\tilde{\tilde{H}} = -\hbar\omega_1 \frac{1}{2} \begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix}$$

Density matrix evolved under this Hamiltonian, is given by:

$$\rho(t)=\frac{1}{2}\begin{bmatrix}3&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-3\end{bmatrix}+\left(-i\omega_1 t\right)\frac{1}{2}\begin{bmatrix}0&-\sqrt{3}&0&0\\\sqrt{3}&0&-2&0\\0&2&0&-\sqrt{3}\\0&0&\sqrt{3}&0\end{bmatrix}+\frac{\left(-i\omega_1 t\right)^2}{2!}\frac{1}{2}\begin{bmatrix}3&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-3\end{bmatrix}+\frac{\left(-i\omega_1 t\right)^3}{3!}\frac{1}{2}.$$

$$\begin{bmatrix}0&-\sqrt{3}&0&0\\\sqrt{3}&0&-2&0\\0&2&0&-\sqrt{3}\\0&0&\sqrt{3}&0\end{bmatrix}+\frac{\left(-i\omega_1 t\right)^4}{4!}\frac{1}{2}\begin{bmatrix}3&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-3\end{bmatrix}+\frac{\left(-i\omega_1 t\right)^5}{5!}\frac{1}{2}\begin{bmatrix}0&-\sqrt{3}&0&0\\\sqrt{3}&0&-2&0\\0&2&0&-\sqrt{3}\\0&0&\sqrt{3}&0\end{bmatrix}+.........$$

$$\Rightarrow \rho(t)=\left\{\left(-i\omega_1 t\right)+\frac{\left(-i\omega_1 t\right)^3}{3!}+\frac{\left(-i\omega_1 t\right)^5}{5!}+\frac{\left(-i\omega_1 t\right)^7}{7!}.......\right\}\frac{1}{2}\begin{bmatrix}0&-\sqrt{3}&0&0\\\sqrt{3}&0&-2&0\\0&2&0&-\sqrt{3}\\0&0&\sqrt{3}&0\end{bmatrix}$$

$$+\left\{1+\frac{\left(-i\omega_1 t\right)^2}{2!}+\frac{\left(-i\omega_1 t\right)^4}{4!}+\frac{\left(-i\omega_1 t\right)^6}{6!}+.....\right\}\frac{1}{2}\begin{bmatrix}3&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-3\end{bmatrix}$$

$$\Rightarrow \quad \rho(t)=Cos\left(\omega_1 t\right)\frac{1}{2}\begin{bmatrix}3&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-3\end{bmatrix}-iSin\left(\omega_1 t\right)\frac{1}{2}\begin{bmatrix}0&-\sqrt{3}&0&0\\\sqrt{3}&0&-2&0\\0&2&0&-\sqrt{3}\\0&0&\sqrt{3}&0\end{bmatrix} \tag{9}$$

$$\left\langle \tilde{\tilde{I}}^{+}\right\rangle = Tr\left[-iSin\left(\omega_1 t\right)\frac{1}{2}\left\{\begin{bmatrix}0&0&-2\sqrt{3}&0\\0&0&0&0\\0&0&4&0\\0&0&0&0\end{bmatrix}+iSin(\omega_Q t)\begin{bmatrix}0&0&0&0\\0&3&0&2\sqrt{3}\\0&0&0&0\\0&0&0&-3\end{bmatrix}+Cos(\omega_Q t)\begin{bmatrix}0&0&0&0\\0&3&0&-2\sqrt{3}\\0&0&0&0\\0&0&0&3\end{bmatrix}\right\}\exp(i\omega_0 t)\right]$$

Maximum intensity is N^2, when $Sin\left(\omega_1 t\right)$ is equal to unity, i.e. $t=\frac{\pi}{2\omega_1}$

$$\Rightarrow \left\langle \tilde{\tilde{I}}^{+}\right\rangle = -iSin\left(\omega_1 t\right)\left\{2+3Cos(\omega_Q t)\right\}\exp(i\omega_0 t) \tag{10}$$

B) Soft Pulse regime

Case 1: Effective Hamiltonian [see eqn. (3.45)] for this matching condition is represented as:

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix}$$

Density matrix evolved under this Hamiltonian, is given by:

$$\rho(t) = \frac{1}{2}\begin{bmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{bmatrix} + \left(-i\omega_1 t\right)\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix} + \frac{\left(-i\omega_1 t\right)^2}{2!}\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & -3 \end{bmatrix} + \frac{\left(-i\omega_1 t\right)^3}{3!}\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -3\sqrt{3} \\ 0 & 0 & 3\sqrt{3} & 0 \end{bmatrix}$$

$$+ \frac{\left(-i\omega_1 t\right)^4}{4!}\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 9 & 0 \\ 0 & 0 & 0 & -9 \end{bmatrix} + \frac{\left(-i\omega_1 t\right)^5}{5!}\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -9\sqrt{3} \\ 0 & 0 & 9\sqrt{3} & 0 \end{bmatrix} + \frac{\left(-i\omega_1 t\right)^6}{6!}\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 27 & 0 \\ 0 & 0 & 0 & -27 \end{bmatrix} + ...$$

$$\Rightarrow \rho(t) = \frac{1}{2}\begin{bmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{bmatrix} + \left\{\left(-\sqrt{3}i\omega_1 t\right) + \frac{\left(-\sqrt{3}i\omega_1 t\right)^3}{3!} + \frac{\left(-\sqrt{3}i\omega_1 t\right)^5}{5!} + ...\right\}\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$$

$$+ \left\{\frac{\left(-\sqrt{3}i\omega_1 t\right)^2}{2!} + \frac{\left(-\sqrt{3}i\omega_1 t\right)^4}{4!} + \frac{\left(-\sqrt{3}i\omega_1 t\right)^6}{6!} + ...\right\}\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$$

$$\Rightarrow \rho(t) = \frac{1}{2}\begin{bmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{bmatrix} - iSin\left(\sqrt{3}\omega_1 t\right)\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{bmatrix} + \left\{Cos\left(\sqrt{3}\omega_1 t\right) - 1\right\}\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \tag{11}$$

$$\left\langle \tilde{\tilde{I}}^+ \right\rangle = Tr\left[-iSin\left(\sqrt{3}\omega_1 t\right)\frac{1}{2}\left\{ iSin(\omega_Q t)\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{3} \end{bmatrix} + Cos(\omega_Q t)\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{3} \end{bmatrix}\right\}\exp(i\omega_0 t)\right]$$

$$\Rightarrow \left\langle \tilde{\tilde{I}}^+ \right\rangle = -\sqrt{3}iSin\left(\sqrt{3}\omega_1 t\right)\frac{1}{2}\left\{-iSin(\omega_Q t) + Cos(\omega_Q t)\right\}\exp(i\omega_0 t) \tag{12}$$

Maximum intensity is $\frac{\sqrt{3}}{2}N^2$, when $Sin\left(\sqrt{3}\omega_1 t\right)$ is equal to unity, i.e. $t = \frac{\pi}{2\sqrt{3}\omega_1}$

Case 2: Effective Hamiltonian [see eqn. (3.46)] for this matching condition is represented as:

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

Density matrix evolved under this Hamiltonian, is given by:

$$\rho(t) = \frac{1}{2}\begin{bmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{bmatrix} + \left(-i\omega_1 t\right)\frac{1}{2}\begin{bmatrix} 0 & -\sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + \frac{\left(-i\omega_1 t\right)^2}{2!}\frac{1}{2}\begin{bmatrix} 3 & 0 & 0 & 0 \\ 0 & -3 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + \frac{\left(-i\omega_1 t\right)^3}{3!}\frac{1}{2}\begin{bmatrix} 0 & -3\sqrt{3} & 0 & 0 \\ 3\sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

$$+ \frac{\left(-i\omega_1 t\right)^4}{4!}\frac{1}{2}\begin{bmatrix} 9 & 0 & 0 & 0 \\ 0 & -9 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + \frac{\left(-i\omega_1 t\right)^5}{5!}\frac{1}{2}\begin{bmatrix} 0 & -9\sqrt{3} & 0 & 0 \\ 9\sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + \frac{\left(-i\omega_1 t\right)^6}{6!}\frac{1}{2}\begin{bmatrix} 27 & 0 & 0 & 0 \\ 0 & -27 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + \ldots\ldots.$$

$$\Rightarrow \rho(t) = \frac{1}{2}\begin{bmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{bmatrix} + \left\{\left(-\sqrt{3}i\omega_1 t\right) + \frac{\left(-\sqrt{3}i\omega_1 t\right)^3}{3!} + \frac{\left(-\sqrt{3}i\omega_1 t\right)^5}{5!} + \ldots\ldots.\right\}\frac{1}{2}\begin{bmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

$$+ \left\{\frac{\left(-\sqrt{3}i\omega_1 t\right)^2}{2!} + \frac{\left(-\sqrt{3}i\omega_1 t\right)^4}{4!} + \frac{\left(-\sqrt{3}i\omega_1 t\right)^6}{6!} + \ldots..\right\}\frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

$$\Rightarrow \rho(t) = \frac{1}{2}\begin{bmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{bmatrix} - iSin\left(\sqrt{3}\omega_1 t\right)\frac{1}{2}\begin{bmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + \left\{Cos\left(\sqrt{3}\omega_1 t\right) - 1\right\}\frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \quad (13)$$

$$\left\langle \tilde{\tilde{I}}^{+} \right\rangle = Tr\left[-iSin\left(\sqrt{3}\omega_1 t\right)\frac{1}{2}\left\{ iSin(\omega_Q t)\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & \sqrt{3} & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + Cos(\omega_Q t)\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & \sqrt{3} & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \right\} \exp(i\omega_0 t) \right]$$

$$\Rightarrow \left\langle \tilde{\tilde{I}}^{+} \right\rangle = -\sqrt{3} iSin\left(\sqrt{3}\omega_1 t\right)\frac{1}{2}\left\{ iSin(\omega_Q t) + Cos(\omega_Q t) \right\} \exp(i\omega_0 t) \qquad (14)$$

Maximum intensity is $\frac{\sqrt{3}}{2}N^2$, when $Sin\left(\sqrt{3}\omega_1 t\right)$ is equal to unity, i.e. $t = \frac{\pi}{2\sqrt{3}\omega_1}$

Case 3: Effective Hamiltonian [see eqn. (3.47)] for this matching condition is represented as:

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

Density matrix evolved under this Hamiltonian, is given by:

$$\rho(t) = \frac{1}{2}\begin{bmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{bmatrix} + \left(-i\omega_1 t\right)\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + \frac{\left(-i\omega_1 t\right)^2}{2!}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & -2 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + \frac{\left(-i\omega_1 t\right)^3}{3!}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & -4 & 0 \\ 0 & 4 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

$$+ \frac{\left(-i\omega_1 t\right)^4}{4!}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 8 & 0 & 0 \\ 0 & 0 & -8 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + \frac{\left(-i\omega_1 t\right)^5}{5!}\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & -16 & 0 \\ 0 & 16 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + \frac{\left(-i\omega_1 t\right)^6}{6!}\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 32 & 0 & 0 \\ 0 & 0 & -32 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + ...$$

$$\Rightarrow \rho(t) = \frac{1}{2}\begin{bmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{bmatrix} + \left\{ \left(-2i\omega_1 t\right) + \frac{\left(-2i\omega_1 t\right)^3}{3!} + \frac{\left(-2i\omega_1 t\right)^5}{5!} + ... \right\}\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

$$+ \left\{ \frac{\left(-2i\omega_1 t\right)^2}{2!} + \frac{\left(-2i\omega_1 t\right)^4}{4!} + \frac{\left(-2i\omega_1 t\right)^6}{6!} + ... \right\}\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

$$\Rightarrow \rho(t) = \frac{1}{2}\begin{bmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{bmatrix} - iSin\left(2\omega_1 t\right)\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + \left\{Cos\left(2\omega_1 t\right) - 1\right\}\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \tag{15}$$

$$\left\langle \tilde{\tilde{I}}^{+} \right\rangle = Tr\left[-iSin\left(2\omega_1 t\right)\frac{1}{2}\left\{ \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + iSin(\omega_Q t)\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} + Cos(\omega_Q t)\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{3} \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \right\} \exp(i\omega_0 t) \right]$$

$$\Rightarrow \left\langle \tilde{\tilde{I}}^{+} \right\rangle = -2iSin\left(2\omega_1 t\right)\frac{1}{2}\exp(i\omega_0 t) \tag{16}$$

Maximum intensity is N^2, when $Sin\left(2\omega_1 t\right)$ is equal to unity, i.e. $t = \frac{\pi}{4\omega_1}$

Appendix 3

Detailed matrix algebra for spin *I* = 5/2

1. Effective RF Hamiltonian

Quadrupolar interaction frame transformation:

$$\tilde{H} = I_X + \left[(3I_Z^2 - I^2), I_X\right](i\phi t) + \left[(3I_Z^2 - I^2), \left[(3I_Z^2 - I^2), I_X\right]\right]\frac{(i\phi t)^2}{2!} + \left[(3I_Z^2 - I^2), \left[(3I_Z^2 - I^2), \left[(3I_Z^2 - I^2) I_X\right]\right]\right]\frac{(i\phi t)^3}{3!} + \dots\dots\dots \quad (1)$$

Employing, above mentioned BCH expansion, Hamiltonian in matrix representation is written as:

$$\tilde{H} = \frac{1}{2}\left\{\begin{bmatrix} 0 & \sqrt{5} & 0 & 0 & 0 & 0 \\ \sqrt{5} & 0 & 2\sqrt{2} & 0 & 0 & 0 \\ 0 & 2\sqrt{2} & 0 & 3 & 0 & 0 \\ 0 & 0 & 3 & 0 & 2\sqrt{2} & 0 \\ 0 & 0 & 0 & 2\sqrt{2} & 0 & \sqrt{5} \\ 0 & 0 & 0 & 0 & \sqrt{5} & 0 \end{bmatrix} + (i\phi t)\begin{bmatrix} 0 & 12\sqrt{5} & 0 & 0 & 0 & 0 \\ -12\sqrt{5} & 0 & 12\sqrt{2} & 0 & 0 & 0 \\ 0 & -12\sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -12\sqrt{2} & 0 \\ 0 & 0 & 0 & 12\sqrt{2} & 0 & -12\sqrt{5} \\ 0 & 0 & 0 & 0 & 12\sqrt{5} & 0 \end{bmatrix} + \frac{(i\phi t)^2}{2!}.\right.$$

$$\begin{bmatrix} 0 & 144\sqrt{5} & 0 & 0 & 0 & 0 \\ 144\sqrt{5} & 0 & 72\sqrt{2} & 0 & 0 & 0 \\ 0 & 72\sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 72\sqrt{2} & 0 \\ 0 & 0 & 0 & 72\sqrt{2} & 0 & 144\sqrt{5} \\ 0 & 0 & 0 & 0 & 144\sqrt{5} & 0 \end{bmatrix} + \frac{(i\phi t)^3}{3!}\begin{bmatrix} 0 & 1728\sqrt{5} & 0 & 0 & 0 & 0 \\ -1728\sqrt{5} & 0 & 432\sqrt{2} & 0 & 0 & 0 \\ 0 & -432\sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -432\sqrt{2} & 0 \\ 0 & 0 & 0 & 432\sqrt{2} & 0 & -1728\sqrt{5} \\ 0 & 0 & 0 & 0 & 1728\sqrt{5} & 0 \end{bmatrix}$$

$$\left. + \frac{(i\phi)^4}{4!}\begin{bmatrix} 0 & 20736\sqrt{5} & 0 & 0 & 0 & 0 \\ 20736\sqrt{5} & 0 & 2592\sqrt{2} & 0 & 0 & 0 \\ 0 & 2592\sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2592\sqrt{2} & 0 \\ 0 & 0 & 0 & 2592\sqrt{2} & 0 & 20736\sqrt{5} \\ 0 & 0 & 0 & 0 & 20736\sqrt{5} & 0 \end{bmatrix} + \dots\dots\dots \right\} \quad (2)$$

Above expression, eqn. (2) is rearranged as:

$$\tilde{H}=\frac{1}{2}\left(\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&3&0&0\\0&0&3&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}+\left\{(12i\phi t)+\frac{(12i\phi t)^3}{3!}+.......\right\}\begin{bmatrix}0&\sqrt{5}&0&0&0&0\\-\sqrt{5}&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&-\sqrt{5}\\0&0&0&0&\sqrt{5}&0\end{bmatrix}\right.$$

$$+\left\{1+\frac{(12i\phi t)^2}{2!}+\frac{(12i\phi t)^4}{4!}...\right\}\begin{bmatrix}0&\sqrt{5}&0&0&0&0\\\sqrt{5}&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&\sqrt{5}\\0&0&0&0&\sqrt{5}&0\end{bmatrix}+\left\{(6i\phi t)+\frac{(6i\phi t)^3}{3!}+..\right\}\begin{bmatrix}0&0&0&0&0&0\\0&0&2\sqrt{2}&0&0&0\\0&-2\sqrt{2}&0&0&0&0\\0&0&0&0&-2\sqrt{2}&0\\0&0&0&2\sqrt{2}&0&0\\0&0&0&0&0&0\end{bmatrix}$$

$$\left.+\left\{1+\frac{(6i\phi t)^2}{2!}+\frac{(6i\phi t)^4}{4!}3^2............\right\}\begin{bmatrix}0&0&0&0&0&0\\0&0&2\sqrt{2}&0&0&0\\0&2\sqrt{2}&0&0&0&0\\0&0&0&0&2\sqrt{2}&0\\0&0&0&2\sqrt{2}&0&0\\0&0&0&0&0&0\end{bmatrix}\right) \tag{3}$$

Using exponential expansion of trigonometric function *Cosine* and *Sine*, eqn. (3) is written as:

$$\tilde{H}=\frac{1}{2}\left(\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&3&0&0\\0&0&3&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}+iSin(12\phi t)\begin{bmatrix}0&\sqrt{5}&0&0&0&0\\-\sqrt{5}&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&-\sqrt{5}\\0&0&0&0&\sqrt{5}&0\end{bmatrix}+Cos(12\phi t)\begin{bmatrix}0&\sqrt{5}&0&0&0&0\\\sqrt{5}&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&\sqrt{5}\\0&0&0&0&\sqrt{5}&0\end{bmatrix}\right.$$

$$\left.+iSin(6\phi t)\begin{bmatrix}0&0&0&0&0&0\\0&0&2\sqrt{2}&0&0&0\\0&-2\sqrt{2}&0&0&0&0\\0&0&0&0&-2\sqrt{2}&0\\0&0&0&2\sqrt{2}&0&0\\0&0&0&0&0&0\end{bmatrix}+Cos(6\phi t)\begin{bmatrix}0&0&0&0&0&0\\0&0&2\sqrt{2}&0&0&0\\0&2\sqrt{2}&0&0&0&0\\0&0&0&0&2\sqrt{2}&0\\0&0&0&2\sqrt{2}&0&0\\0&0&0&0&0&0\end{bmatrix}\right) \tag{4}$$

Zeeman interaction frame transformation: Hamiltonian in Zeeman interaction frame is given by:

$$\tilde{\tilde{H}} = \exp(-i\omega_0 t I_Z)\left\{ \underbrace{\begin{bmatrix} 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&3&0&0\\ 0&0&3&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0 \end{bmatrix}}_{A} + iSin(2\omega_Q t)\underbrace{\begin{bmatrix} 0&\sqrt{5}&0&0&0&0\\ -\sqrt{5}&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&-\sqrt{5}\\ 0&0&0&0&\sqrt{5}&0 \end{bmatrix}}_{B} \right.$$

$$+ Cos(2\omega_Q t)\underbrace{\begin{bmatrix} 0&\sqrt{5}&0&0&0&0\\ \sqrt{5}&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&\sqrt{5}\\ 0&0&0&0&\sqrt{5}&0 \end{bmatrix}}_{C} + iSin(\omega_Q t)\underbrace{\begin{bmatrix} 0&0&0&0&0&0\\ 0&0&2\sqrt{2}&0&0&0\\ 0&-2\sqrt{2}&0&0&0&0\\ 0&0&0&0&-2\sqrt{2}&0\\ 0&0&0&2\sqrt{2}&0&0\\ 0&0&0&0&0&0 \end{bmatrix}}_{D}$$

$$\left. + Cos(\omega_Q t)\underbrace{\begin{bmatrix} 0&0&0&0&0&0\\ 0&0&2\sqrt{2}&0&0&0\\ 0&2\sqrt{2}&0&0&0&0\\ 0&0&0&0&2\sqrt{2}&0\\ 0&0&0&2\sqrt{2}&0&0\\ 0&0&0&0&0&0 \end{bmatrix}}_{E} \right\} \exp(i\omega_0 t I_Z)\left\{-\hbar\omega_1 \cos(\omega_{rf} t)\right\} \qquad (5)$$

Solution for above expression is obtained by employing BCH expansion mentioned below:

$$\tilde{\tilde{H}} = X + [Y, X](i\omega_0 t) + [Y,[Y,X]]\frac{(i\omega_0 t)^2}{2!} + [Y,[Y,[Y,X]]]\frac{(i\omega_0 t)^3}{3!} + ... \qquad (6)$$

Action of I_Z on Matrix A of eqn. (5) is given as follows:

$$\begin{bmatrix} 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&3&0&0\\ 0&0&3&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0 \end{bmatrix} + (i\phi t)\begin{bmatrix} 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&3&0&0\\ 0&0&-3&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0 \end{bmatrix} + \frac{(i\phi t)^2}{2!}.\begin{bmatrix} 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&3&0&0\\ 0&0&3&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0 \end{bmatrix} +$$

$$+\frac{(i\phi t)^3}{3!}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&3&0&0\\0&0&-3&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}+\frac{(i\phi t)^4}{4!}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&3&0&0\\0&0&3&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}++\frac{(i\phi t)^5}{5!}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&3&0&0\\0&0&-3&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}.........$$

Close solution for above expression after splitting the matrices is given as:

$$\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&3&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}\exp(i\omega_0 t)+\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&3&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}\exp(-i\omega_0 t) \tag{7a}$$

Action of I_Z on Matrix B of eqn. (5) is given as follows:

$$\begin{bmatrix}0&\sqrt{5}&0&0&0&0\\-\sqrt{5}&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&-\sqrt{5}\\0&0&0&0&\sqrt{5}&0\end{bmatrix}+(i\phi t)\begin{bmatrix}0&\sqrt{5}&0&0&0&0\\\sqrt{5}&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&-\sqrt{5}\\0&0&0&0&-\sqrt{5}&0\end{bmatrix}+\frac{(i\phi t)^2}{2!}.\begin{bmatrix}0&\sqrt{5}&0&0&0&0\\\sqrt{5}&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&-\sqrt{5}\\0&0&0&0&-\sqrt{5}&0\end{bmatrix}$$

$$+\frac{(i\phi t)^3}{3!}\begin{bmatrix}0&\sqrt{5}&0&0&0&0\\-\sqrt{5}&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&-\sqrt{5}\\0&0&0&0&\sqrt{5}&0\end{bmatrix}+\frac{(i\phi t)^4}{4!}\begin{bmatrix}0&\sqrt{5}&0&0&0&0\\\sqrt{5}&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&-\sqrt{5}\\0&0&0&0&-\sqrt{5}&0\end{bmatrix}+...$$

Since lower diagonals alternatively change the polarity, so matrices are splitted and close solution is given by:

$$\begin{bmatrix}0&\sqrt{5}&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&-\sqrt{5}\\0&0&0&0&0&0\end{bmatrix}\exp(i\omega_0 t)+\begin{bmatrix}0&0&0&0&0&0\\-\sqrt{5}&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&\sqrt{5}&0\end{bmatrix}\exp(-i\omega_0 t) \tag{7b}$$

Action of I_Z on Matrix C of eqn. (5) is given as follows:

$$\begin{bmatrix} 0 & \sqrt{5} & 0 & 0 & 0 & 0 \\ \sqrt{5} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \sqrt{5} \\ 0 & 0 & 0 & 0 & \sqrt{5} & 0 \end{bmatrix} + (i\phi t)\begin{bmatrix} 0 & \sqrt{5} & 0 & 0 & 0 & 0 \\ -\sqrt{5} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\sqrt{5} \\ 0 & 0 & 0 & 0 & -\sqrt{5} & 0 \end{bmatrix} + \frac{(i\phi t)^2}{2!}.\begin{bmatrix} 0 & \sqrt{5} & 0 & 0 & 0 & 0 \\ \sqrt{5} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \sqrt{5} \\ 0 & 0 & 0 & 0 & \sqrt{5} & 0 \end{bmatrix}$$

$$+ \frac{(i\phi t)^3}{3!}\begin{bmatrix} 0 & \sqrt{5} & 0 & 0 & 0 & 0 \\ -\sqrt{5} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \sqrt{5} \\ 0 & 0 & 0 & 0 & -\sqrt{5} & 0 \end{bmatrix} + \frac{(i\phi t)^4}{4!}\begin{bmatrix} 0 & \sqrt{5} & 0 & 0 & 0 & 0 \\ \sqrt{5} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \sqrt{5} \\ 0 & 0 & 0 & 0 & \sqrt{5} & 0 \end{bmatrix} + ...$$

Again lower diagonals changes the polarity, so close solution is given by splitting the matrices as following:

$$\begin{bmatrix} 0 & \sqrt{5} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \sqrt{5} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \exp(i\omega_0 t) + \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ \sqrt{5} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \sqrt{5} & 0 \end{bmatrix} \exp(-i\omega_0 t) \quad (7c)$$

Action of I_Z on Matrix D of eqn. (5) is given as follows:

$$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2\sqrt{2} & 0 & 0 & 0 \\ 0 & -2\sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -2\sqrt{2} & 0 \\ 0 & 0 & 0 & 2\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} + (i\phi t)\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2\sqrt{2} & 0 & 0 & 0 \\ 0 & 2\sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -2\sqrt{2} & 0 \\ 0 & 0 & 0 & -2\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} + \frac{(i\phi t)^2}{2!}.\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2\sqrt{2} & 0 & 0 & 0 \\ 0 & -2\sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -2\sqrt{2} & 0 \\ 0 & 0 & 0 & 2\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} +$$

$$+\frac{(i\phi t)^3}{3!}\begin{bmatrix}0&0&0&0&0&0\\0&0&2\sqrt{2}&0&0&0\\0&2\sqrt{2}&0&0&0&0\\0&0&0&0&-2\sqrt{2}&0\\0&0&0&-2\sqrt{2}&0&0\\0&0&0&0&0&0\end{bmatrix}+\frac{(i\phi t)^4}{4!}\begin{bmatrix}0&0&0&0&0&0\\0&0&2\sqrt{2}&0&0&0\\0&-2\sqrt{2}&0&0&0&0\\0&0&0&0&-2\sqrt{2}&0\\0&0&0&2\sqrt{2}&0&0\\0&0&0&0&0&0\end{bmatrix}+\ ...$$

Close solution after splitting the matrices is given as:

$$\begin{bmatrix}0&0&0&0&0&0\\0&0&2\sqrt{2}&0&0&0\\0&0&0&0&0&0\\0&0&0&0&-2\sqrt{2}&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}\exp(i\omega_0 t)+\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&-2\sqrt{2}&0&0&0&0\\0&0&0&0&0&0\\0&0&0&2\sqrt{2}&0&0\\0&0&0&0&0&0\end{bmatrix}\exp(-i\omega_0 t) \tag{7d}$$

Action of I_Z on Matrix E of eqn. (5) is given as follows:

$$\begin{bmatrix}0&0&0&0&0&0\\0&0&2\sqrt{2}&0&0&0\\0&2\sqrt{2}&0&0&0&0\\0&0&0&0&2\sqrt{2}&0\\0&0&0&2\sqrt{2}&0&0\\0&0&0&0&0&0\end{bmatrix}+(i\phi t)\begin{bmatrix}0&0&0&0&0&0\\0&0&2\sqrt{2}&0&0&0\\0&-2\sqrt{2}&0&0&0&0\\0&0&0&0&2\sqrt{2}&0\\0&0&0&-2\sqrt{2}&0&0\\0&0&0&0&0&0\end{bmatrix}+\frac{(i\phi t)^2}{2!}.\begin{bmatrix}0&0&0&0&0&0\\0&0&2\sqrt{2}&0&0&0\\0&2\sqrt{2}&0&0&0&0\\0&0&0&0&2\sqrt{2}&0\\0&0&0&2\sqrt{2}&0&0\\0&0&0&0&0&0\end{bmatrix}$$

$$+\frac{(i\phi t)^3}{3!}\begin{bmatrix}0&0&0&0&0&0\\0&0&2\sqrt{2}&0&0&0\\0&-2\sqrt{2}&0&0&0&0\\0&0&0&0&2\sqrt{2}&0\\0&0&0&-2\sqrt{2}&0&0\\0&0&0&0&0&0\end{bmatrix}+\frac{(i\phi t)^4}{4!}\begin{bmatrix}0&0&0&0&0&0\\0&0&2\sqrt{2}&0&0&0\\0&-2\sqrt{2}&0&0&0&0\\0&0&0&0&2\sqrt{2}&0\\0&0&0&-2\sqrt{2}&0&0\\0&0&0&0&0&0\end{bmatrix}+....$$

Close solution of above expression by splitting the matrices is given as:

$$\begin{bmatrix}0&0&0&0&0&0\\0&0&2\sqrt{2}&0&0&0\\0&0&0&0&0&0\\0&0&0&0&2\sqrt{2}&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}\exp(i\omega_0 t)+\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&2\sqrt{2}&0&0&0&0\\0&0&0&0&0&0\\0&0&0&2\sqrt{2}&0&0\\0&0&0&0&0&0\end{bmatrix}\exp(-i\omega_0 t) \tag{7e}$$

Using results of eqn. (7), solution of eqn. (5) is given as:

$$
\begin{aligned}
\tilde{\tilde{H}} = \left\{-\hbar\omega_1 \cos(\omega_{rf} t)\right\} \Bigg\{ & \left(\begin{bmatrix} 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&3&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0 \end{bmatrix} \exp(i\omega_0 t) + \begin{bmatrix} 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&3&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0 \end{bmatrix} \exp(-i\omega_0 t) \right) \\
& + i\left\{Sin(2\omega_Q t)\right\} \left(\begin{bmatrix} 0&\sqrt{5}&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&-\sqrt{5}\\ 0&0&0&0&0&0 \end{bmatrix} \exp(i\omega_0 t) + \begin{bmatrix} 0&0&0&0&0&0\\ -\sqrt{5}&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&\sqrt{5}&0 \end{bmatrix} \exp(-i\omega_0 t) \right) \\
& + \{Cos(2\omega_Q t)\} \left(\begin{bmatrix} 0&\sqrt{5}&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&\sqrt{5}\\ 0&0&0&0&0&0 \end{bmatrix} \exp(i\omega_0 t) + \begin{bmatrix} 0&0&0&0&0&0\\ \sqrt{5}&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&\sqrt{5}&0 \end{bmatrix} \exp(-i\omega_0 t) \right) \\
& + i\left\{Sin(\omega_Q t)\right\} \left(\begin{bmatrix} 0&0&0&0&0&0\\ 0&0&2\sqrt{2}&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&-2\sqrt{2}&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0 \end{bmatrix} \exp(i\omega_0 t) + \begin{bmatrix} 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&-2\sqrt{2}&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&2\sqrt{2}&0&0\\ 0&0&0&0&0&0 \end{bmatrix} \exp(-i\omega_0 t) \right) \Bigg\} \qquad (8)
\end{aligned}
$$

2. Evolution of density matrix

Evolved density matrix under effective Hamiltonian is obtained by:

$$\rho(t) = \rho(0) + \left(\frac{i}{\hbar} t\right)\left[H, \rho(0)\right] + \frac{1}{2!}\left(\frac{i}{\hbar} t\right)^2 \left[H, \left[H, \rho(0)\right]\right] + ...$$

The initial density matrix for spin-5/2 nuclei is given by:

$$\tilde{\tilde{\rho}}(0)=\frac{1}{2}\begin{bmatrix}5&0&0&0&0&0\\0&3&0&0&0&0\\0&0&1&0&0&0\\0&0&0&-1&0&0\\0&0&0&0&-3&0\\0&0&0&0&0&5\end{bmatrix}$$

A) Hard pulse regime: Effective Hamiltonian [see eqn. (3.58)] is represented as:

$$\tilde{\tilde{H}}=-\hbar\omega_1\frac{1}{2}\begin{bmatrix}0&\sqrt{5}&0&0&0&0\\\sqrt{5}&0&2\sqrt{2}&0&0&0\\0&2\sqrt{2}&0&3&0&0\\0&0&3&0&2\sqrt{2}&0\\0&0&0&2\sqrt{2}&0&\sqrt{5}\\0&0&0&0&\sqrt{5}&0\end{bmatrix}$$

Density matrix evolved under this Hamiltonian, is given by:

$$\rho(t)=\frac{1}{2}\begin{bmatrix}5&0&0&0&0&0\\0&3&0&0&0&0\\0&0&1&0&0&0\\0&0&0&-1&0&0\\0&0&0&0&-3&0\\0&0&0&0&0&5\end{bmatrix}+\left(-i\omega_1 t\right)\frac{1}{2}\begin{bmatrix}0&-\sqrt{5}&0&0&0&0\\\sqrt{5}&0&-2\sqrt{2}&0&0&0\\0&2\sqrt{2}&0&-3&0&0\\0&0&3&0&-2\sqrt{2}&0\\0&0&0&2\sqrt{2}&0&-\sqrt{5}\\0&0&0&0&\sqrt{5}&0\end{bmatrix}$$

$$+\frac{\left(-i\omega_1 t\right)^2}{2!}\frac{1}{2}\begin{bmatrix}5&0&0&0&0&0\\0&3&0&0&0&0\\0&0&1&0&0&0\\0&0&0&-1&0&0\\0&0&0&0&-3&0\\0&0&0&0&0&5\end{bmatrix}+\frac{\left(-i\omega_1 t\right)^3}{3!}\frac{1}{2}\begin{bmatrix}0&-\sqrt{5}&0&0&0&0\\\sqrt{5}&0&-2\sqrt{2}&0&0&0\\0&2\sqrt{2}&0&-3&0&0\\0&0&3&0&-2\sqrt{2}&0\\0&0&0&2\sqrt{2}&0&-\sqrt{5}\\0&0&0&0&\sqrt{5}&0\end{bmatrix}$$

$$+\frac{\left(-i\omega_1 t\right)^4}{4!}\frac{1}{2}\begin{bmatrix}5&0&0&0&0&0\\0&3&0&0&0&0\\0&0&1&0&0&0\\0&0&0&-1&0&0\\0&0&0&0&-3&0\\0&0&0&0&0&5\end{bmatrix}+\frac{\left(-i\omega_1 t\right)^5}{5!}\frac{1}{2}\begin{bmatrix}0&-\sqrt{5}&0&0&0&0\\\sqrt{5}&0&-2\sqrt{2}&0&0&0\\0&2\sqrt{2}&0&-3&0&0\\0&0&3&0&-2\sqrt{2}&0\\0&0&0&2\sqrt{2}&0&-\sqrt{5}\\0&0&0&0&\sqrt{5}&0\end{bmatrix}+\ldots\ldots\ldots$$

$$\Rightarrow \rho(t) = Cos\left(\omega_1 t\right)\frac{1}{2}\begin{bmatrix} 5 & 0 & 0 & 0 & 0 & 0 \\ 0 & 3 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -3 & 0 \\ 0 & 0 & 0 & 0 & 0 & 5 \end{bmatrix} - iSin\left(\omega_1 t\right)\frac{1}{2}\begin{bmatrix} 0 & -\sqrt{5} & 0 & 0 & 0 & 0 \\ \sqrt{5} & 0 & -2\sqrt{2} & 0 & 0 & 0 \\ 0 & 2\sqrt{2} & 0 & -3 & 0 & 0 \\ 0 & 0 & 3 & 0 & -2\sqrt{2} & 0 \\ 0 & 0 & 0 & 2\sqrt{2} & 0 & -\sqrt{5} \\ 0 & 0 & 0 & 0 & \sqrt{5} & 0 \end{bmatrix} \tag{9}$$

$$\left\langle \tilde{\tilde{I}}^{+} \right\rangle = Tr\begin{bmatrix} -iSin\left(\omega_1 t\right)\frac{1}{2}\left\{\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -6\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 9 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} + iSin(2\omega_Q t)\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 5 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 2\sqrt{10} \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -5 \end{bmatrix}\right. \\ +\left\{Cos(2\omega_Q t) - 1/2\right\}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 5 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -2\sqrt{10} \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 5 \end{bmatrix} + iSin(\omega_Q t)\begin{bmatrix} 0 & 0 & -2\sqrt{10} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 8 & 0 & 6\sqrt{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -8 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \\ \left. +\left\{Cos(\omega_Q t) - 1/2\right\}\begin{bmatrix} 0 & 0 & -2\sqrt{10} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 8 & 0 & -6\sqrt{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 8 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}\right\}\exp(i\omega_0 t) \end{bmatrix}$$

$$\left\langle \tilde{\tilde{I}}^{+} \right\rangle = -iSin\left(\omega_1 t\right)\left\{\frac{9}{2}e^{i\omega_0 t} + 5\frac{e^{i2\omega_Q t + i\omega_0 t} + e^{-i2\omega_Q t + i\omega_0 t}}{2} + 8\frac{e^{i\omega_Q t + i\omega_0 t} + e^{-i\omega_Q t + i\omega_0 t}}{2}\right\} \tag{10}$$

B) Soft Pulse regime

Case 1: Effective Hamiltonian [see eqn. (3.60)] for this matching condition is represented as:

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2\sqrt{2} & 0 & 0 & 0 \\ 0 & 2\sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

Density matrix evolved under this Hamiltonian, is given by:

$$\rho(t)=\frac{1}{2}\begin{bmatrix}5&0&0&0&0&0\\0&3&0&0&0&0\\0&0&1&0&0&0\\0&0&0&-1&0&0\\0&0&0&0&-3&0\\0&0&0&0&0&5\end{bmatrix}+\left(-i\omega_1 t\right)\begin{bmatrix}0&0&0&0&0&0\\0&0&-\sqrt{2}&0&0&0\\0&\sqrt{2}&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}+\frac{\left(-i\omega_1 t\right)^2}{2!}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&4&0&0&0\\0&0&0&-4&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}$$

$$+\frac{\left(-i\omega_1 t\right)^3}{3!}\begin{bmatrix}0&0&0&0&0&0\\0&0&-8\sqrt{2}&0&0&0\\0&8\sqrt{2}&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}+\frac{\left(-i\omega_1 t\right)^4}{4!}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&32&0&0&0\\0&0&0&-32&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}$$

$$+\frac{\left(-i\omega_1 t\right)^5}{5!}\begin{bmatrix}0&0&0&0&0&0\\0&0&-64\sqrt{2}&0&0&0\\0&64\sqrt{2}&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}+\frac{\left(-i\omega_1 t\right)^6}{6!}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&256&0&0&0\\0&0&0&-256&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}+.......$$

$$\rho(t)=\frac{1}{2}\begin{bmatrix}5&0&0&0&0&0\\0&3&0&0&0&0\\0&0&1&0&0&0\\0&0&0&-1&0&0\\0&0&0&0&-3&0\\0&0&0&0&0&5\end{bmatrix}-iSin\left(2\sqrt{2}\omega_1 t\right)\frac{1}{2}\begin{bmatrix}0&0&0&0&0&0\\0&0&-1&0&0&0\\0&1&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}+\left\{Cos\left(2\sqrt{2}\omega_1 t\right)-1\right\}\frac{1}{2}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&1&0&0&0\\0&0&0&-1&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix} \quad (11)$$

$$\left\langle \tilde{\tilde{I}}^{+}\right\rangle = Tr\left[-iSin\left(2\sqrt{2}\omega_1 t\right)\frac{1}{2}\left\{i\left\{Sin(\omega_Q t)\right\}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&2\sqrt{2}&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}+\{Cos(\omega_Q t)-1/2\}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&2\sqrt{2}&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}\right\}\exp(i\omega_0 t)\right]$$

$$\Rightarrow \left\langle \tilde{\tilde{I}}^{+}\right\rangle = -\sqrt{2}iSin\left(2\sqrt{2}\omega_1 t\right)\left\{i\left\{Sin(\omega_Q t)\right\}+\{Cos(\omega_Q t)-1/2\}\exp(i\omega_0 t)\right. \quad (12)$$

Case 2: Effective Hamiltonian [see eqn. (3.61)] for this matching condition is represented as:

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2\sqrt{2} & 0 \\ 0 & 0 & 0 & 2\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

Density matrix evolved under this Hamiltonian, is given by:

$$\rho(t) = \frac{1}{2}\begin{bmatrix} 5 & 0 & 0 & 0 & 0 & 0 \\ 0 & 3 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -3 & 0 \\ 0 & 0 & 0 & 0 & 0 & 5 \end{bmatrix} + \left(-i\omega_1 t\right)\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\sqrt{2} & 0 \\ 0 & 0 & 0 & \sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} + \frac{\left(-i\omega_1 t\right)^2}{2!}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 4 & 0 & 0 \\ 0 & 0 & 0 & 0 & -4 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$+ \frac{\left(-i\omega_1 t\right)^3}{3!}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -8\sqrt{2} & 0 \\ 0 & 0 & 0 & 8\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} + \frac{\left(-i\omega_1 t\right)^4}{4!}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 32 & 0 & 0 \\ 0 & 0 & 0 & 0 & -32 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$+ \frac{\left(-i\omega_1 t\right)^5}{5!}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -64\sqrt{2} & 0 \\ 0 & 0 & 0 & 64\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} + \frac{\left(-i\omega_1 t\right)^6}{6!}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 256 & 0 & 0 \\ 0 & 0 & 0 & 0 & -256 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} + ...$$

$$\Rightarrow \rho(t) = \frac{1}{2}\begin{bmatrix} 5 & 0 & 0 & 0 & 0 & 0 \\ 0 & 3 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -3 & 0 \\ 0 & 0 & 0 & 0 & 0 & 5 \end{bmatrix} - iSin\left(2\sqrt{2}\omega_1 t\right)\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} + \left\{Cos\left(2\sqrt{2}\omega_1 t\right) - 1\right\}\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (13)$$

$$\left\langle \tilde{\tilde{I}}^{+} \right\rangle = Tr\left[-iSin\left(2\sqrt{2}\omega_1 t\right)\left\{ i\left\{Sin(\omega_Q t)\right\}\begin{bmatrix} 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&-2\sqrt{2}&0\\ 0&0&0&0&0&0 \end{bmatrix} + \{Cos(\omega_Q t)-1/2\}\begin{bmatrix} 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&2\sqrt{2}&0\\ 0&0&0&0&0&0 \end{bmatrix}\right\}\exp(i\omega_0 t) \right]$$

$$\Rightarrow \left\langle \tilde{\tilde{I}}^{+} \right\rangle = -\sqrt{2}iSin\left(2\sqrt{2}\omega_1 t\right)\left\{-i\left\{Sin(\omega_Q t)\right\} + \{Cos(\omega_Q t)-1/2\}\exp(i\omega_0 t)\right. \qquad (14)$$

Case 3: Effective Hamiltonian [see eqn. (3.62)] for this matching condition is represented as:

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\begin{bmatrix} 0&\sqrt{5}&0&0&0&0\\ \sqrt{5}&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0 \end{bmatrix}$$

Density matrix evolved under this Hamiltonian, is given by:

$$\rho(t) = \frac{1}{2}\begin{bmatrix} 5&0&0&0&0&0\\ 0&3&0&0&0&0\\ 0&0&1&0&0&0\\ 0&0&0&-1&0&0\\ 0&0&0&0&-3&0\\ 0&0&0&0&0&5 \end{bmatrix} + \left(-i\omega_1 t\right)\frac{1}{2}\begin{bmatrix} 0&-\sqrt{5}&0&0&0&0\\ \sqrt{5}&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0 \end{bmatrix} + \frac{\left(-i\omega_1 t\right)^2}{2!}\frac{1}{2}\begin{bmatrix} 5&0&0&0&0&0\\ 0&-5&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0 \end{bmatrix}$$

$$+\frac{\left(-i\omega_1 t\right)^3}{3!}\frac{1}{2}\begin{bmatrix} 0&-5\sqrt{5}&0&0&0&0\\ 5\sqrt{5}&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0 \end{bmatrix} + \frac{\left(-i\omega_1 t\right)^4}{4!}\frac{1}{2}\begin{bmatrix} 25&0&0&0&0&0\\ 0&-25&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0 \end{bmatrix}$$

$$+\frac{\left(-i\omega_1 t\right)^5}{5!}\frac{1}{2}\begin{bmatrix} 0&-25\sqrt{5}&0&0&0&0\\ 25\sqrt{5}&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0 \end{bmatrix} + \frac{\left(-i\omega_1 t\right)^6}{6!}\frac{1}{2}\begin{bmatrix} 125&0&0&0&0&0\\ 0&-125&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0 \end{bmatrix} + \ldots..$$

$$\Rightarrow \rho(t)=\frac{1}{2}\begin{bmatrix}5&0&0&0&0&0\\0&3&0&0&0&0\\0&0&1&0&0&0\\0&0&0&-1&0&0\\0&0&0&0&-3&0\\0&0&0&0&0&5\end{bmatrix}-iSin\left(\sqrt{5}\omega_1 t\right)\frac{1}{2}\begin{bmatrix}0&-1&0&0&0&0\\1&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}+\left\{Cos\left(\sqrt{5}\omega_1 t\right)-1\right\}\frac{1}{2}\begin{bmatrix}1&0&0&0&0&0\\0&-1&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix} \quad (15)$$

$$\left\langle \tilde{\tilde{I}}^{+}\right\rangle = Tr\left[-iSin\left(\sqrt{5}\omega_1 t\right)\frac{1}{2}\left\{i\left\{Sin(2\omega_Q t)\right\}\begin{bmatrix}0&0&0&0&0&0\\0&\sqrt{5}&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}+\{Cos(2\omega_Q t)-1/2\}\begin{bmatrix}0&0&0&0&0&0\\0&\sqrt{5}&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}\right\}\exp(i\omega_0 t)\right]$$

$$\Rightarrow \left\langle \tilde{\tilde{I}}^{+}\right\rangle = -\frac{\sqrt{5}}{2} iSin\left(\sqrt{5}\omega_1 t\right)\left\{i\left\{Sin(2\omega_Q t)\right\}+\{Cos(2\omega_Q t)-1/2\}\exp(i\omega_0 t)\right. \quad (16)$$

Case 4: Effective Hamiltonian [see eqn. (63)] for this matching condition is represented as:

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&\sqrt{5}\\0&0&0&0&\sqrt{5}&0\end{bmatrix}$$

Density matrix evolved under this Hamiltonian, is given by:

$$\rho(t)=\frac{1}{2}\begin{bmatrix}5&0&0&0&0&0\\0&3&0&0&0&0\\0&0&1&0&0&0\\0&0&0&-1&0&0\\0&0&0&0&-3&0\\0&0&0&0&0&5\end{bmatrix}+\left(-i\omega_1 t\right)\frac{1}{2}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&-\sqrt{5}\\0&0&0&0&\sqrt{5}&0\end{bmatrix}+\frac{\left(-i\omega_1 t\right)^2}{2!}\frac{1}{2}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&5&0\\0&0&0&0&0&-5\end{bmatrix}+\frac{\left(-i\omega_1 t\right)^3}{3!}\frac{1}{2}\cdot$$

$$\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&-5\sqrt{5}\\0&0&0&0&5\sqrt{5}&0\end{bmatrix}+\frac{\left(-i\omega_1 t\right)^4}{4!}\frac{1}{2}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&25&0\\0&0&0&0&0&-25\end{bmatrix}+\frac{\left(-i\omega_1 t\right)^5}{5!}\frac{1}{2}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&-25\sqrt{5}\\0&0&0&0&25\sqrt{5}&0\end{bmatrix}+\ldots.$$

$$\Rightarrow \rho(t)=\frac{1}{2}\begin{bmatrix}5&0&0&0&0&0\\0&3&0&0&0&0\\0&0&1&0&0&0\\0&0&0&-1&0&0\\0&0&0&0&-3&0\\0&0&0&0&0&5\end{bmatrix}-iSin\left(\sqrt{5}\omega_1 t\right)\frac{1}{2}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&-1\\0&0&0&0&1&0\end{bmatrix}+\left\{Cos\left(\sqrt{5}\omega_1 t\right)-1\right\}\frac{1}{2}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&1&0\\0&0&0&0&0&-1\end{bmatrix} \tag{17}$$

$$\left\langle \tilde{\tilde{I}}^{+}\right\rangle = Tr\left[-iSin\left(\sqrt{5}\omega_1 t\right)\frac{1}{2}\left\{i\left\{Sin(2\omega_Q t)\right\}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&-\sqrt{5}\end{bmatrix}+\{Cos(2\omega_Q t)-1/2\}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&\sqrt{5}\end{bmatrix}\right\}\exp(i\omega_0 t)\right]$$

$$\Rightarrow \left\langle \tilde{\tilde{I}}^{+}\right\rangle = -\frac{\sqrt{5}}{2} iSin\left(\sqrt{5}\omega_1 t\right)\left\{-i\left\{Sin(2\omega_Q t)\right\}+\{Cos(2\omega_Q t)-1/2\}\exp(i\omega_0 t)\right. \tag{18}$$

Case 5: Effective Hamiltonian [see eqn. (3.64)] for this matching condition is represented as:

$$\tilde{\tilde{H}} = -\frac{\hbar\omega_1}{2}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&3&0&0\\0&0&3&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}$$

Density matrix evolved under this Hamiltonian, is given by:

$$\rho(t)=\frac{1}{2}\begin{bmatrix}5&0&0&0&0&0\\0&3&0&0&0&0\\0&0&1&0&0&0\\0&0&0&-1&0&0\\0&0&0&0&-3&0\\0&0&0&0&0&5\end{bmatrix}+\left(-i\omega_1 t\right)\frac{1}{2}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&-3&0&0\\0&0&3&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}+\frac{\left(-i\omega_1 t\right)^2}{2!}\frac{1}{2}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&9&0&0&0\\0&0&0&-9&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}+\frac{\left(-i\omega_1 t\right)^3}{3!}\frac{1}{2}\cdot$$

$$\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&-27&0&0\\0&0&27&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}+\frac{\left(-i\omega_1 t\right)^4}{4!}\frac{1}{2}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&81&0&0&0\\0&0&0&-81&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}+\frac{\left(-i\omega_1 t\right)^5}{5!}\frac{1}{2}\begin{bmatrix}0&0&0&0&0&0\\0&0&0&0&0&0\\0&0&0&-243&0&0\\0&0&243&0&0&0\\0&0&0&0&0&0\\0&0&0&0&0&0\end{bmatrix}+....$$

$$\Rightarrow \rho(t) = \frac{1}{2}\begin{bmatrix} 5 & 0 & 0 & 0 & 0 & 0 \\ 0 & 3 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -3 & 0 \\ 0 & 0 & 0 & 0 & 0 & 5 \end{bmatrix} + \left\{ \left(-3i\omega_1 t\right) + \frac{\left(-3i\omega_1 t\right)^3}{3!} + \frac{\left(-3i\omega_1 t\right)^5}{5!} + ... \right\} \frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$+ \left\{ \frac{\left(-3i\omega_1 t\right)^2}{2!} + \frac{\left(-3i\omega_1 t\right)^4}{4!} + \frac{\left(-3i\omega_1 t\right)^6}{6!} + ... \right\} \frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$\Rightarrow \rho(t) = \frac{1}{2}\begin{bmatrix} 5 & 0 & 0 & 0 & 0 & 0 \\ 0 & 3 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -3 & 0 \\ 0 & 0 & 0 & 0 & 0 & 5 \end{bmatrix} - iSin\left(3\omega_1 t\right)\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} + \left\{Cos\left(3\omega_1 t\right) - 1\right\}\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (19)$$

$$\left\langle \tilde{\tilde{I}}^{+} \right\rangle = Tr\left[-iSin\left(3\omega_1 t\right)\frac{1}{2}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 3 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \exp(i\omega_0 t) \right]$$

$$\Rightarrow \left\langle \tilde{\tilde{I}}^{+} \right\rangle = -\frac{3}{2} iSin\left(3\omega_1 t\right)\exp(i\omega_0 t) \quad (20)$$