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Applications of Floquet-Magnus and Fer Expansion Approaches during Cross Polarization Radiation in Solid State NMR

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Abstract

This paper investigates the concept of Cross Polarization (CP) experiment in addition to revisiting the two potential expansion schemes recently developed in the field of solid-state nuclear magnetic resonance (SSNMR): namely, the Floquet-Magnus expansion and the Fer expansion. We use the aforementioned expansion schemes for the calculation of effective Hamiltonians and propagators when the spin system undergoes Cross Polarization radiation. CP is the gateway experiment into SSNMR. An in-depth comprehension of the underlying mechanics of spin dynamics during the cross-polarization experiment is pivotal for further experimental developments and optimization of more complex solid-state NMR experiments. The main contribution of this work is a prospect related to spin physics; particularly regarding to generalization of the calculation. This work reports original yet interesting novel ideas and developments that include calculations performed on the CP experiment. In fact, the approach presented could play a major role in the interpretation of several fine NMR experiments in solids, which would in turn provide significant new insights in spin physics. The generality of the work points towards potential applications in problems related in solid-state NMR and theoretical developments of spectroscopy as well as interdisciplinary research areas as long as they include spin dynamics concepts.

Keywords

Cross Polarization, Solid-State NMR, Floquet-Magnus Expansion, Fer Expansion, Spin Dynamics

1. Introduction

Solid-state NMR (SSNMR) is an advancement of NMR spectroscopy often characterized by the presence of anisotropic interactions. There have been tremendous advancements, particularly with regard to spin dynamics. To be specific, the introduction of the Floquet-Magnus expansion (FME) [1] [2] [3] and Fer expansion (FE) [4] [5] [6] approaches as alternative schemes to the main approaches; *i.e.*, the average Hamiltonian theory (AHT) [7]-[28] and the Floquet theory (FLT) [29] [30] [31] [32], has greatly revolutionized this field. Basically, these recently introduced approaches aim at solving a time-dependent linear differential equation that is inclined towards obtaining propagators.

For a long time, theoretical investigations have been pivotal in solid-state NMR assessment since the early days of the field and have retained their relevance even when investigating multi-pulse NMR, magic-angle spinning NMR [33] [34], multiple quantum NMR as well as to the general field of spin dynamics. Although FME and FE are different approximations of the same equation, the results of the formal expression of the effective Hamiltonian they provide differ in higher orders of expansion. In recent years, there has been a surge in interest in these two approaches, particularly when investigating various physics systems such as topological materials [35]. Detailed applications of these approaches to many different SSNMR problems are important and useful in SSNMR as well as in the general field of spectroscopy. Comprehension of spin dynamics is fundamental to the development of pulse techniques for the transfer of spin polarization [14]. In this article, we applied the FME and FE approaches to a specific well-known SSNMR experiment called Cross Polarization (CP) [33], which generally involve transfer of spin polarization from one spin species to another, leading to the common observation of NMR signals. The results reported for each approach will facilitate discovery of the most efficient scheme that possesses better performance, regarding creation of expressions that are easier to implement when calculating spin evolution. The presence of the commutators in the calculation of the propagator $U(\tau_C)_{Fer}$; for instance, when using the Baker-Campbell-Hausdorff (BCH) [36], dictates that the rate of convergence of the FE is slower than that of the FME from the computation effectiveness point of view. The Baker-Campbell-Hausdorff formula [36] about the exponential function of two operators, X and Y, and their commutator $[X, Y]$ is written as,

$$e^X e^Y = e^{X+Y+\frac{1}{2}[X,Y]+\frac{1}{12}[X,[X,Y]]-\frac{1}{12}[Y,[X,Y]]+\cdots}. \tag{1}$$

By applying the above formula (Equation (1)) to the FE, we can write the first two expansion terms of FE as [36]

$$U(\tau_C)_{Fer} = e^{-i\tau_C \overline{H_{Fer}^{(0)}}} e^{-i\tau_C \overline{H_{Fer}^{(1,0)}}} = e^{-i\tau_C \overline{H_{Fer}^{(0)}} - i\tau_C \overline{H_{Fer}^{(1,0)}} + \frac{1}{2}(-i\tau_C)^2 \left[\overline{H_{Fer}^{(0)}}, \overline{H_{Fer}^{(1,0)}}\right] + \cdots} \tag{2}$$

where $U(\tau_C)_{Fer}$ is the expression of the Fer propagator for a time period τ_C. $\overline{H_{Fer}^{(0)}}$ and $\overline{H_{Fer}^{(1,0)}}$ are the first and second order of the Fer expansion, respectively. One appealing feature of the FME is to give a formal expression of the

Floquet Hamiltonian [35]. Arguably, the starting point of the FME is to expand the propagator in the form of the time evolution operator [2]

$$U(t) = P(t)\mathrm{e}^{-itF} P^{+}(0). \tag{3}$$

The operator $P(t)$ introduces the frame of the density operator varying under the time-independent Hamiltonian F. F is expanded in powers of the Fourier transform of the Hamiltonian and can also be transformed in powers of the perturbation. On the other hand, the Fer expansion remarkable point may be that it expands a propagator in the form of a product of propagators with nth-order Hamiltonians as

$$U(t) = \prod_{n=0}^{\infty} \exp\{-iF_n(t)\}. \tag{4}$$

This form of propagator allows evaluation of the time-evolution governed by the 1st-order Hamiltonian separately from those by higher order Hamiltonians. This paper examines the average Hamiltonians and propagators of the two expansion schemes (FME and FE) for Cross Polarization experiment [33]. In these investigations, we found some subtle differences between the FME and FE schemes that could definitely lead to a close relationship between the FE and the FME. The FME is obtained by representing the solution of the time dependent Schrödinger equation

$$\frac{\mathrm{d}U(t)}{\mathrm{d}t} = -iHU(t) \tag{5}$$

in the form of Equation (3) and using the following exponential ansatz

$$P(t) = \exp\{-i\Lambda(t)\}, \tag{6}$$

where the function $\Lambda(t)$ ($\Lambda(t) = \sum_n \Lambda_n(t)$) is the argument of the operator $P(t)$. These lead to the modified form of the Magnus expansion [1] [2]. In its form, the FME starts as the FE by introducing a first exponential factor. This raises the question if

$$\Lambda(t) = F_1(t). \tag{7}$$

When solving problems of spin dynamics in solids, the FME appears to be more suitable than the FE. The FE's apparent complexity (lengthy calculation of the commutators borne from the BCH formula) necessitates more input computationally when compared to the FME. From the computational effectiveness, this tells us that the rate of convergence of the FME is faster than that of the FE, for a prescribed precision; therefore, one needs more $\Lambda_n's$ (FE) than $F_k's$ (FME). Regardless, they are some cases such as spin system in the three-level system [21] where this result is reverse. As such, one can conclude that the characteristics of the problem at hand tend to dictate the method to be used. This kind of performance influences numerical simulations of new pulse-technique development. The best approach could be considered as a theory of choice not only to describe and explain SSNMR results, but also to design, develop, and improve several pulse sequences involving the CP sequence. The best approach (FME

or FE) found could also be subject to a potential candidate of developing advanced spin evolution software to simulate SSNMR experiments. Driven by demands of the experimental NMR, numerous computer programs, including SPINACH (based on Matlab) [37], SIMPSON (based on scripting interface, Tcl) [38], and SPINEVOLUTION (based on Chebyshev polynomial expansion) [39], have been developed over the past few decades for the simulation of NMR experiments. Against this backdrop, the avenue of new computer programs is still a welcome idea for simulations in SSNMR. Even so, the development of advanced spin evolution software using either the FME or the FE approach is not the goal of this paper.

In essence, the Fer expansion was developed as an alternative to the Magnus expansion and is still in its early stage in applications in both classical and modern physics [40]. On the other hand, hitherto, the FME has been employed frequently for the treatment of quantum Floquet systems which open new possibilities to control quantum systems [1] [36] [41] [42] [43]. This approach is practically useful for the high-frequency driving, in which the higher-order contribution is not relevant to dynamics at short time scale. However, in the case of finite frequencies, the problem is more intricate since, in general; the FME is not a convergent series expansion in the thermodynamic limit. More discussions on the physical meaning of the FME and FE including an interesting recent work by Takegoshi and co-workers can be found in the literature [44]-[52]. Due to the successes of AHT and FLT in designing a plethora of experiments in solid-state NMR, the investigation of new or alternative approaches such as FME and FE is important as it might improve or lead to new methodological progress in spin dynamics.

This paper is organized as follows. In section II, we applied the FME and FE to the CP experiment. In section III, we put the work in a prospect of spin physics to make the calculation more general. Finally, section IV presents our conclusions.

2. Application of FME and FE to Cross Polarization

The key point may be realized if we compare the propagators with the 0th and 1st-order average Hamiltonians,

$$U(\tau_C) \approx \exp\left\{-i\tau_C\left(\bar{H}_{FME}^{(0)} + \bar{H}_{FME}^{(1)}\right)\right\} \tag{8}$$

and

$$U(\tau_C) \approx \exp\left\{-i\tau_C\bar{H}_{FE}^{(0)}\right\}\exp\left\{-i\tau_C\bar{H}_{FE}^{(1)}\right\}. \tag{9}$$

In general, the above two exponentials are not equivalent unless the experiments present certain physical particularities, such as the CW decoupling and the rotary resonance recoupling, which are of particular interest in NMR. The general formula for the FME are given by

$$\Lambda_n(t) = \Lambda_n(0) + \int_0^t G_n(\tau)\,\mathrm{d}\tau - tF_n, \tag{10}$$

with

$$F_n = \frac{1}{T}\int_0^T G_n(\tau)\,\mathrm{d}\tau. \tag{11}$$

where the first three orders are given by

$$G_1(\tau) = \tilde{H}(\tau), \tag{12}$$

$$G_2(\tau) = -\frac{i}{2}\left[\tilde{H}(\tau) + F_1, \Lambda_1(\tau)\right], \tag{13}$$

$$\begin{aligned} G_3(\tau) = &-\frac{i}{2}\left[\tilde{H}(\tau) + F_1, \Lambda_2(\tau)\right] - \frac{i}{2}\left[F_2, \Lambda_1(\tau)\right] \\ &-\frac{1}{12}\left[\Lambda_1(\tau), \left[\Lambda_1(\tau), \tilde{H}(\tau) - F_1\right]\right]. \end{aligned} \tag{14}$$

2.1. Application of FME to Cross Polarization

Let us consider the truncated Hamiltonian for the heteronuclear dipolar coupled two spins under double RF irradiation on both the $\boldsymbol{I}$ and $\boldsymbol{S}$ spin at "on resonance" is given by [50]

$$H = dI_Z S_Z + \omega_1 I_X + \omega_1 S_X \tag{15}$$

where d is the heteronuclear dipolar interaction and ω_1 is the intensity of RF irradiation along the X axis. The frequencies of the two spins I and S are the same because when both spins are on resonance, and when the spin-lock fields are chosen appropriately, the Hartman-condition described on appendix 2 is fulfilled (Equation (90)). The relevant Hamiltonian in the interaction frame defined by

$$U_{rf}(t) = \exp\left\{-i\omega_1 (I_X + S_X)t\right\} \tag{16}$$

becomes

$$\tilde{H}(t) = \frac{d}{2}\left\{I_Z S_Z + I_Y S_Y + (I_Y S_Z + I_Z S_Y)\sin 2\omega_1 t + (I_Z S_Z - I_Y S_Y)\cos 2\omega_1 t\right\}. \tag{17}$$

Note that the effect of MAS on the spin-lattice relaxation is negligeable [53]. The first order contribution to the FME gives F_1 and $\Lambda_1(t)$ obtained below,

$$F_1 = \frac{d}{2}(I_Z S_Z + I_Y S_Y), \tag{18}$$

and

$$\Lambda_1(t) = -\frac{d}{4\omega_1}(\cos(2\omega_1 t) - 1)(I_Y S_Z + I_Z S_Y) + \frac{d}{4\omega_1}\sin(2\omega_1 t)(I_Z S_Z - I_Y S_Y). \tag{19}$$

The second order contribution to the FME, F_2, can be calculate by the integral

$$F_2 = \frac{1}{T}\int_0^T G_2(\tau)\,\mathrm{d}\tau, \tag{20}$$

which gives the result,

$$F_2 = -\frac{id^2}{8\omega_1}\left[I_Z S_Z + I_Y S_Y, I_Y S_Z + I_Z S_Y\right]. \tag{21}$$

After rearrangement, we have

$$F_2 = \frac{d^2}{8\omega_1}\left[I_X\left(S_Y^2 - S_Z^2\right) + \left(I_Y^2 - I_Z^2\right)S_X\right], \tag{22}$$

where the function, $G_2(\tau)$, is calculated in the appendix. The $\Lambda_2(t)$ contribution can also be heavily calculated with the following formula obtained from the above general Equation (10).

$$\Lambda_2(t) = \Lambda_2(0) - \frac{i}{2}\int_0^t \left[H(\tau), \Lambda_1(\tau)\right] \mathrm{d}\tau - tF_2. \tag{23}$$

A tedious calculation presented in the appendix gives

$$\begin{aligned}\Lambda_2(t) = \frac{id^2}{16\omega_1}\Bigg\{ & C_1\left[\frac{1}{8\omega_1} + \alpha_1(t)\right] - C_2\left[\alpha_2(t)\right] + C_3\left[\alpha_3(t)\right] \\ & - C_4\left[\frac{1}{8\omega_1} + \alpha_4(t)\right] - 2C_5\left[\frac{1}{2\omega_1} + \alpha_5(t)\right] + 2C_6\left[\alpha_6(t)\right]\Bigg\},\end{aligned} \tag{24}$$

where the commutators $C_1, C_2, C_3, \cdots$ and C_6, and the functions $\alpha_1, \alpha_2, \alpha_3, \cdots$ and α_6 are given in the appendix.

The calculation of F_3 is performed with

$$F_3 = \frac{1}{T}\int_0^T G_3(\tau)\mathrm{d}\tau, \tag{25}$$

where

$$G_3(t) = -\frac{i}{2}\left[H(t) + F_1, \Lambda_2(t)\right] - \frac{i}{2}\left[F_2, \Lambda_1(t)\right] - \frac{1}{12}\left[\Lambda_1(t), \left[\Lambda_1(t), H(t) - F_1\right]\right]. \tag{26}$$

The function $G_3(t)$ is calculated in the appendix and we found

$$\begin{aligned}G_3(t) = & \frac{d^3}{64\omega_1^2}\left[I_Z S_Z + I_Y S_Y, \frac{C_1}{4} - \frac{C_4}{4} - 2C_5\right] - \frac{i}{2} f_3(t) \\ & + \frac{d^3}{64\omega_1^2}\left[I_Y S_Z + I_Z S_Y, C_6\right] - \frac{i}{2} f_1(t) - \frac{1}{12} f_2(t),\end{aligned} \tag{27}$$

where the functions $f_1(t)$, $f_2(t)$, and $f_3(t)$ are given in the appendix. The integration of the function $G_3(t)$ yield

$$F_3 = \frac{d^3}{64\omega_1^2}\left\{\left[I_Z S_Z + I_Y S_Y, \frac{C_1}{4} - \frac{C_4}{4} - 2C_5\right] + \left[I_Y S_Z + I_Z S_Y, C_6\right]\right\}. \tag{28}$$

It can, obviously, be seen that the magnitude of F_3 is of the order of $\approx \frac{d^3}{64\omega_1^2}$. Higher-order contributions to the FME can also be obtained after lengthy calculations, but results are not presented here.

2.2. Application of FE to Cross Polarization

We verified the results calculated in reference [50] for the first three orders average Hamiltonians in the Fer expansion for the heteronuclear dipolar coupled two spins under double RF irradiation on both I and S spin at "on resonance". The results obtained are given here,

$$\overline{H_{Fer}^{(0)}} = \frac{d}{2}\left(I_Z S_Z + I_Y S_Y\right) \tag{29}$$

$$\overline{H_{Fer}^{(1,0)}} = \frac{d^2}{16\omega_1}\left(I_X + S_X\right) \tag{30}$$

$$\overline{H_{Fer}^{(1,1)}} = \frac{d^3}{64\omega_1^2}\left(I_Z S_Z - I_Y S_Y\right) \tag{31}$$

For the CP experiment, the first order contribution to the FME (F_1) and to the FE ($\overline{H_{Fer}^{(0)}}$) are identical. The second order of both expansions (FME and FE) is different and the dissimilarity due to spins contributions is present in the results of the second-order contribution of the two expansions. The spin contribution in the 2nd-order FME is given by the Equation (21), while the spin contribution for the 2nd-order FE is given by the Equation (30). The bilinear terms in the second-order contribution of the FME (Equation (21)) due to the spin's contribution can be understood as a polarization transfer mechanism from spin $\boldsymbol{I}$ to spin $\boldsymbol{S}$. In this respect, the FME can be considered to be the right expansion scheme to utilize for CP experiment because it displays bilinear term contributions of spin systems that are not obtained in the second-order contribution of the Fer expansion $\overline{H_{Fer}^{(1,0)}}$. The bilinear terms appear, instead, in the third-order contribution of the Fer expansion (Equation (31)).

Let us recall that the cross-polarization methodology was introduced to the NMR community in 1973 by Pines, Gibby, and Waugh [33] for the detection of rare spins in high-resolution solid-state NMR. Following the indirect detection schemes of Hartmann and Hahn [54], and of Lurie and Slichter [55], Pines and co-worker [33] integrated these CP methods with high-power spin decoupling and inaugurated one of the most important techniques that advocate and advance solid-state NMR spectroscopy on low-abundance spins. The combination of cross polarization, magic angle spinning, and heteronuclear decoupling is now the routine experimental method for recording high-resolution NMR spectra of spin-1/2 nuclei. The results for CP using the Fer expansion were obtained by simple inspection of the evolution propagator. The heavy calculations to obtain the FME terms compared to the obtention of the Fer expansion terms make the FE more favorable to be used for the CP experiment. Thus, the Fer expansion is more appropriated to appreciate effects of time-evolution under Hamiltonians with different orders separately, compared to the FME approach because of the easier way of Fer expansion calculation of the average Hamiltonians. Again, as mentioned above for the heteronuclear dipolar decoupling, the characteristics of the problem at hand might ultimately dictate the approach to be utilized for the CP experiments as well.

3. Spin Physics

In order to make the calculation more general, we can write the Hamiltonian in the following form,

$$H(t) = \omega_S S_X + \omega_I I_X + d I_Z S_Z \tag{32}$$

In the RF interaction frame, the Hamiltonian becomes

$$\tilde{H}^{Y}(t) = d\{I_X \cos(\omega_I t) + I_Y \sin(\omega_I t)\}\{S_X \cos(\omega_S t) + S_Y \sin(\omega_S t)\} \tag{33}$$

The Hartmann-Hahn condition [54], allows to write

$$\tilde{H}^{Y}(t) = d\{I_X \cos(\omega_1 t) + I_Y \sin(\omega_1 t)\}\{S_X \cos(\omega_1 t) + S_Y \sin(\omega_1 t)\} \tag{34}$$

$$\begin{aligned}\tilde{H}^{Y}(t) = &\frac{d}{2}(I_X S_X + I_Y S_Y) + \frac{d}{2}(I_X S_X - I_Y S_Y)\cos(2\omega_1 t) \\ &+ \frac{d}{2}(I_X S_Y + I_Y S_X)\sin(2\omega_1 t)\end{aligned} \tag{35}$$

$$H_0^Y = \frac{d}{2}(I_X S_X + I_Y S_Y) \tag{36}$$

$$H_{+2}^Y = \frac{d}{2}(I_X S_X - I_Y S_Y) - i\frac{d}{2}(I_X S_Y + I_Y S_X) \tag{37}$$

$$H_{-2}^Y = \frac{d}{2}(I_X S_X - I_Y S_Y) + i\frac{d}{2}(I_X S_Y + I_Y S_X) \tag{38}$$

Let us introduce the fictitious spin spaces as follows,

$$I_{Z,DQ} = \frac{1}{2}(S_Z + I_Z) \tag{39}$$

$$I_{X,DQ} = \frac{1}{2}(S_+ I_+ + S_- I_-) = S_X I_X - S_Y I_Y \tag{40}$$

$$I_{Y,DQ} = -\frac{i}{2}(S_+ I_+ - S_- I_-) = S_X I_Y + S_Y I_X \tag{41}$$

$$I_{Z,ZQ} = \frac{1}{2}(S_Z - I_Z) \tag{42}$$

$$I_{X,ZQ} = \frac{1}{2}(S_+ I_- + S_- I_+) = S_X I_X + S_Y I_Y \tag{43}$$

$$I_{Y,ZQ} = -\frac{i}{2}(S_+ I_- - S_- I_+) = S_X I_Y - S_Y I_X \tag{44}$$

with

$$[I_{a,ZQ}, I_{b,DQ}] = 0 \tag{45}$$

$$\tilde{H}^{Y}(t) = \frac{d}{2} I_{X,ZQ} + \frac{d}{2} I_{X,DQ} \cos(2\omega_1 t) + \frac{d}{2} I_{Y,DQ} \sin(2\omega_1 t) \tag{46}$$

One of the most intriguing NMR experiments is the excitation of transitions which contravenes the selection rule $\Delta m = \pm 1$, that is to say, for $I = 1/2$ nuclei, where more than one spin participates in the transition. New detection methods make it possible to observe Double Quantum (DQ) or multiple-quantum transitions in a convenient way. Zero-quantum (ZQ) transitions are particularly interesting, since they were not detected by early continuous-wave techniques due to their insensitivity to magnet in homogeneity broadening [56]. A single quantum transition is the most common transition that creates magnetization in

the transverse plane with a single spin change state. With a simultaneous shift of both spins, it is possible to obtain either zero quantum (the spins flip to opposite states) or double quantum (spins flip the same way) transitions. Figure 1 shows the typical spin transitions for a spin system, IS. Double-quantum coherence connects the states $|\alpha\alpha>$ and $|\beta\beta>$ and zero-quantum coherence connects states $|\alpha\beta>$ and $|\beta\alpha>$. This principle can be rationalized using the energy level diagram [57].

In the vector model, double quantum transitions have no magnetization in the transverse plane and only transverse magnetization can be observed. But, DQ transition can be transferred to single quantum transition through the process of generation of first pulse, evolution and generation of multiple quantum coherence (second pulse) in a multi quantum experiment.

$$H_0^Y = \frac{d}{2} I_{X,ZQ} \tag{47}$$

$$H_{+2}^Y = \frac{d}{4} I_{-,ZQ} \tag{48}$$

$$H_{-2}^Y = \frac{d}{4} I_{+,ZQ} \tag{49}$$

$$\Lambda_1(t) = \frac{d}{4\omega_1}\left(I_{-,DQ}\mathrm{e}^{+i2\omega_1 t} + I_{+,DQ}\mathrm{e}^{-i2\omega_1 t}\right) \tag{50}$$

$$\Lambda_1(0) = \frac{d}{4\omega_1} I_{X,DQ} = \theta I_{X,DQ} \tag{51}$$

$$F_1 = \frac{d}{2} I_{X,ZQ} \tag{52}$$

$$F_2 = \omega_1 \left(\frac{d}{4\omega_1}\right)^2 I_{Z,DQ} \tag{53}$$

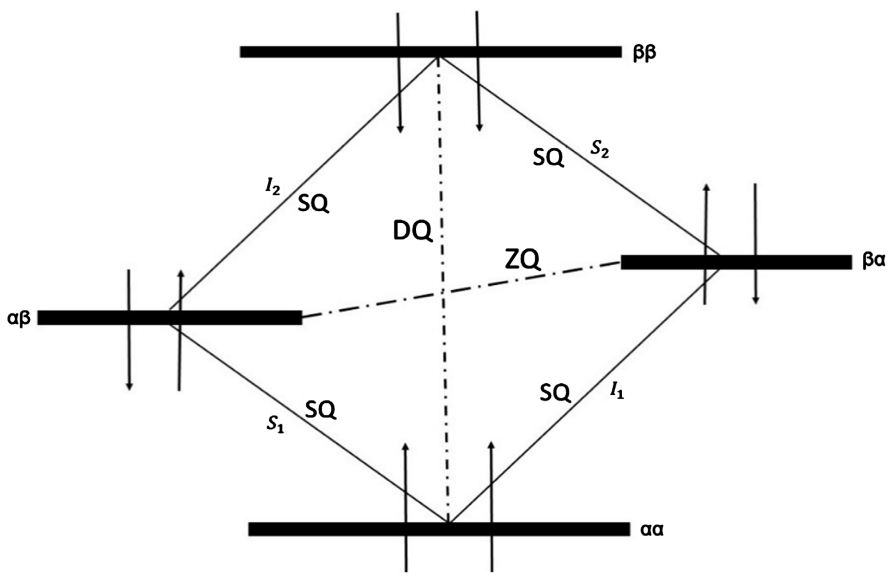

Figure 1. Typical spin transitions for a spin system, I and S.

To second order, the propagator can thus be written as,

$$U(\tau_C,0)=\mathrm{e}^{i\theta I_{X,DQ}}\exp\left(-i\left\{\frac{d}{2}I_{X,ZQ}+\omega_1\left(\frac{d}{4\omega_1}\right)^2 I_{Z,DQ}\right\}\tau_C\right)\mathrm{e}^{-i\theta I_{X,DQ}}=\mathrm{e}^{-i\bar{H}\tau_C} \quad (54)$$

with

$$\bar{H}=\frac{d}{2}I_{X,ZQ}-\omega_1\left(\frac{d}{4\omega_1}\right)^2 I_{Z,DQ}\cos\theta-\sin\theta I_{X,DQ} \quad (55)$$

Thus, the FULL propagator (*i.e.*, in the rotating frame) is

$$U(\tau_C,0)=\mathrm{e}^{-2i\omega_1 I_{Z,DQ}\tau_C}\mathrm{e}^{i\theta I_{X,DQ}}\exp\left(-i\left\{\frac{d}{2}I_{X,ZQ}-\omega_1\left(\frac{d}{4\omega_1}\right)^2 I_{Z,DQ}\right\}\tau_C\right)\mathrm{e}^{-i\theta I_{X,DQ}} \quad (56)$$

Interestingly, with the FE, we can describe separately, by subsequent evolution, the effect of the RF field (locking field) and dipolar interaction, which is, to some extent, one of the aims of the Fer expansion. In addition, at the Hartmann-Hahn condition, all the evolution takes place in the DQ space (up to second order), which characterizes the conservation of the total magnetization during the CP process. Indeed, the CP experiment between a low-abundance ($\boldsymbol{S}$) spin system and a high-abundance spin system ($\boldsymbol{I}$) can be most conveniently described by ignoring the dipolar interaction between the S spins. Vega and co-worker [58] presented an illuminating theory for CP NMR of non-spinning and spinning samples.

Indeed, this section is a presentation of the two-spin CP spin dynamics, commonly used to explain CP-NMR. The above Equation (32) should be written on the form:

$$H^t(t)=\omega_S S_z+\omega_I I_z+dI_xS_x\,. \quad (57)$$

When the spin-lock fields are chosen appropriately, the Hartman-condition described on appendix 2 is fulfilled (Equation (90)) and both frequencies of I and S become the same. In the interaction frame at the Hartmann-Hahn [54] condition, we thus get:

$$H_i^t(t)=\frac{d}{2}\left(I_xS_x+I_yS_y\right)+\frac{d}{2}\left\{\left(I_xS_x-I_yS_y\right)\cos 2\omega_1 t+\left(I_xS_y+I_yS_x\right)\sin 2\omega_1 t\right\} \quad (58)$$

and with the transformation:

$$H_i^t(t)=\exp\left(-i2\omega_1 I_{z,DQ}t\right)H^t(t)\exp\left(i2\omega_1 I_{z,DQ}t\right), \quad (59)$$

this becomes indeed Equation (46)

$$H_i^t(t)=\frac{d}{2}I_{x,ZQ}+\frac{d}{2}\left\{I_{x,DQ}\cos 2\omega_1 t+I_{y,DQ}\sin 2\omega_1 t\right\}. \quad (60)$$

The discussion about the ZQ and DQ transitions makes sense only when the two-spin system itself is discussed. It would be helpful to mention that the system at the start after the first 90˚ pulse is in a state

$$\sigma_i^t(0) = AS_z = \frac{A}{2}\{(S_z + I_z) + (S_z - I_z)\} = \frac{A}{2}\{I_{z,DQ} + I_{z,ZQ}\}. \tag{61}$$

and that according to the commutation relation in Equation (45) and the form of Equation (46):

$$U_i^t(t_c) = U_{i,ZQ}^t(t_c) U_{i,DQ}^t(t_c), \tag{62}$$

where $U_{i\,ZQ}^t(t)$ is straightforward equal to $\exp\{-it_c(d/2\,I_{x,ZQ})\}$. The $U_{i\,DQ}^t(t)$, using the derivation around the Equations (47)-(55), has a form of the DQ operators in Equation (54). In general, we assume during CP that $d \ll \omega_1$ and therefore

$$U_{i\,DQ}^t \approx 1. \tag{63}$$

Thus,

$$U_i^t(t_c) \approx \exp\left\{-it_c \frac{d}{2} I_{x,ZQ}\right\}, \tag{64}$$

and with the above approximation

$$\sigma_i^t(t) \approx \frac{A}{2} I_{z,DQ} + \frac{A}{2}\{I_{z,ZQ}\cos(d/2)t - I_{y,ZQ}\sin(d/2)t\} \tag{65}$$

and

$$\sigma^t(t_c) = \sigma_i^t(t_c) \tag{66}$$

Thus, back to the rotating frame, using

$$I_{z,DQ} = \frac{1}{2}(S_z + I_z) \tag{67}$$

and

$$I_{z,ZQ} = \frac{1}{2}(S_z - I_z), \tag{68}$$

$$\sigma(t_c) = \frac{A}{2}\left\{S_x\left(1 + \cos\frac{d}{2}t_c\right) + I_x\left(1 - \cos\frac{d}{2}t_c\right)\right\} + \cdots \tag{69}$$

showing what CP in fact is doing.

4. Conclusion

This study successfully applies FME and FE during Cross Polarization radiation experiment in SSNMR and subsequently probes the spin dynamics using both approaches. The CP was characterized by the mechanism of polarization transfers from ^{1}H to low-gamma nuclei, X (^{13}C). The characterization shows the matching condition called Hartmann-Hahn [54], a popular concept within the scientific community. Additionally, the study proposed a model of spin physics to interpret the spin dynamics based on a more general calculation. At the Hartmann-Hahn condition, all the evolution takes place in the DQ space, which characterizes the conservation of the total magnetization during the CP process. It is worth stressing that, this is the first attempt to use the FME and FE approaches to investigate the spin dynamics in CP experiment. Therefore, in order to im-

prove the current study and confirm our results, an in-depth comprehension of the CP experiment is necessary. One possible approach would be to add a further theoretical step, such as the fusion of the Floquet-Magnus and Fer expansion approaches. As long as many of these steps can be further improved, future CP experiments are certainly feasible; which will largely benefit from this current development of spin dynamics. This contribution is not impossible, although it is difficult to quantify at this moment. The comparison between FME and FE results gave us an indication of the approach to be utilized for the CP experiment, in particular for the computational point of view. This pilot study shows that the FME is a promising approach to the study of CP experiment and other major SSNMR experiments such as the phase-modulated Lee-Goldburg [59] decoupling where the analysis of spin-systems is currently under investigation. The understanding of spin dynamics during the CP experiment is very useful for further experimental developments and optimization for more complex solid-state NMR experiments. Therefore, this work potentially represents an interesting contribution to the field of NMR spectroscopy.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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Appendix

A1. Floquet-Magnus Expansion Calculation

$$\begin{aligned}
&G_2(t)\\
&=\frac{id^2}{16\omega_1}\Big\{\Big[\big\{I_ZS_Z+I_YS_Y+(I_YS_Z+I_ZS_Y)\sin(2\omega_1 t)+(I_ZS_Z-I_YS_Y)\cos(2\omega_1 t)\big\},\\
&\quad(I_YS_Z+I_ZS_Y)\big(\cos(2\omega_1 t)-1\big)-(I_ZS_Z-I_YS_Y)\sin(2\omega_1 t)\Big]\\
&\quad+\Big[I_ZS_Z+I_YS_Y,(I_YS_Z+I_ZS_Y)\big(\cos(2\omega_1 t)-1\big)-(I_ZS_Z-I_YS_Y)\sin(2\omega_1 t)\Big]\Big\}
\end{aligned} \tag{70}$$

$$\begin{aligned}
&\Lambda_2(t)\\
&=\frac{id^2}{16\omega_1}\int_0^t\Big\{\Big[(I_YS_Z+I_ZS_Y)\sin(2\omega_1\tau)+(I_ZS_Z-I_YS_Y)\cos(2\omega_1\tau),\\
&\quad(I_YS_Z+I_ZS_Y)\big(\cos(2\omega_1\tau)-1\big)-(I_ZS_Z-I_YS_Y)\sin(2\omega_1\tau)\Big]\\
&\quad+\Big[(I_ZS_Z+I_YS_Y),(I_YS_Z+I_ZS_Y)\big(\cos(2\omega_1\tau)-1\big)-(I_ZS_Z-I_YS_Y)\sin(2\omega_1\tau)\Big]\\
&\quad+\Big[(I_ZS_Z+I_YS_Y),(I_YS_Z+I_ZS_Y)\big(\cos(2\omega_1\tau)-1\big)-(I_ZS_Z-I_YS_Y)\sin(2\omega_1\tau)\Big]\Big\}\,\mathrm{d}\tau
\end{aligned} \tag{71}$$

$$\begin{aligned}
&=\frac{id^2}{16\omega_1}\Big\{C_1\int_0^t\sin(2\omega_1\tau)\big(\cos(2\omega_1\tau)-1\big)\mathrm{d}\tau-C_2\int_0^t\sin^2(2\omega_1\tau)\mathrm{d}\tau\\
&\quad+C_3\int_0^t\cos(2\omega_1\tau)\big(\cos(2\omega_1\tau)-1\big)\mathrm{d}\tau-C_4\int_0^t\cos(2\omega_1\tau)\sin(2\omega_1\tau)\mathrm{d}\tau\\
&\quad-2C_5\int_0^t\sin(2\omega_1\tau)\mathrm{d}\tau+2C_6\int_0^t\cos(2\omega_1\tau)\mathrm{d}\tau\Big\}
\end{aligned} \tag{72}$$

where the respective commutators are:

$$C_1=[I_YS_Z+I_ZS_Y,I_YS_Z+I_ZS_Y], \tag{73-a}$$

$$C_2=[I_YS_Z+I_ZS_Y,I_ZS_Z-I_YS_Y], \tag{73-b}$$

$$C_3=[I_ZS_Z-I_YS_Y,I_YS_Z+I_ZS_Y], \tag{73-c}$$

$$C_4=[I_ZS_Z-I_YS_Y,I_ZS_Z-I_YS_Y], \tag{73-d}$$

$$C_5=[I_ZS_Z+I_YS_Y,I_ZS_Z-I_YS_Y], \tag{73-e}$$

$$C_6=[I_ZS_Z+I_YS_Y,I_YS_Z+I_ZS_Y]. \tag{73-f}$$

After integration of the above Equation (72), we obtain

$$\begin{aligned}
\Lambda_2(t)=\frac{id^2}{16\omega_1}\Big\{&C_1\left[\frac{1}{8\omega_1}+\alpha_1(t)\right]-C_2[\alpha_2(t)]+C_3[\alpha_3(t)]\\
&-C_4\left[\frac{1}{8\omega_1}+\alpha_4(t)\right]-2C_5\left[\frac{1}{2\omega_1}+\alpha_5(t)\right]+2C_6[\alpha_6(t)]\Big\},
\end{aligned} \tag{74}$$

where

$$\alpha_1(t)=\frac{-1}{8\omega_1}\cos(4\omega_1 t)-t, \tag{75-a}$$

$$\alpha_2(t)=\frac{1}{2}\left(t-\frac{1}{4\omega_1}\sin(4\omega_1 t)\right), \tag{75-b}$$

$$\alpha_3(t)=\frac{1}{2}\left(t+\frac{1}{4\omega_1}\sin(4\omega_1 t)\right)-\frac{1}{2\omega_1}\sin(2\omega_1 t), \tag{75-c}$$

$$\alpha_4(t)=\frac{-1}{8\omega_1}\cos(4\omega_1\tau), \tag{75-d}$$

$$\alpha_5(t)=\frac{-1}{2\omega_1}\cos(2\omega_1\tau), \tag{75-e}$$

$$\alpha_6(t)=\frac{1}{2\omega_1}\sin(2\omega_1\tau), \tag{75-f}$$

Let us write

$$G_3(t)=-\frac{i}{2}G_{31}(t)-\frac{i}{2}G_{32}(t)-\frac{1}{12}G_{33}(t), \tag{76}$$

$$\begin{aligned}
G_{31}(t)&=\left[\tilde{H}(t)+F_1,\Lambda_2(t)\right]\\
&=\left[\frac{d}{2}\left\{I_Z S_Z+I_Y S_Y+(I_Y S_Z+I_Z S_Y)\sin(2\omega_1 t)+(I_Z S_Z-I_Y S_Y)\cos(2\omega_1 t)\right\}\right.\\
&\quad\left.+\frac{d}{2}(I_Z S_Z+I_Y S_Y),\frac{id^2}{16\omega_1}\left\{C_1\left[\frac{1}{8\omega_1}+\alpha_1(t)\right]-C_2\left[\alpha_2(t)\right]+C_3\left[\alpha_3(t)\right]\right.\right.\\
&\quad\left.\left.-C_4\left[\frac{1}{8\omega_1}+\alpha_4(t)\right]-2C_5\left[\frac{1}{2\omega_1}+\alpha_5(t)\right]+2C_6\left[\alpha_6(t)\right]\right\}\right]\\
&=\frac{id^3}{32\omega_1^2}\left[I_Z S_Z+I_Y S_Y,\frac{C_1}{4}-\frac{C_4}{4}-2C_5\right]+f_3(t),
\end{aligned} \tag{77}$$

$$\begin{aligned}
G_{32}(t)&=\left[F_2,\Lambda_1(t)\right]\\
&=\left[\frac{-id^2}{8\omega_1}C_6,\frac{-d}{4\omega_1}(I_Y S_Z+I_Z S_Y)(\cos(2\omega_1 t)-1)+\frac{d}{4\omega_1}(I_Z S_Z-I_Y S_Y)\sin(2\omega_1 t)\right]\\
&=\frac{id^3}{32\omega_1^2}\left[I_Y S_Z+I_Z S_Y,C_6\right]+f_1(t),
\end{aligned} \tag{78}$$

$$\begin{aligned}
G_{33}(t)&=\left[\Lambda_1(t),\left[\Lambda_1(t),\tilde{H}(t)-F_1\right]\right]\\
&=\left[\Lambda_1(t),\left[\Lambda_1(t),\frac{d}{2}(I_Y S_Z+I_Z S_Y)\sin(2\omega_1 t)+\frac{d}{2}(I_Z S_Z-I_Y S_Y)\cos(2\omega_1 t)\right]\right]\\
&=f_2(t).
\end{aligned} \tag{79}$$

After rearrangement, we obtain

$$\begin{aligned}
G_3(t)&=\frac{d^3}{64\omega_1^2}\left[I_Z S_Z+I_Y S_Y,\frac{C_1}{4}-\frac{C_4}{4}-2C_5\right]-\frac{i}{2}f_3(t)\\
&\quad+\frac{d^3}{64\omega_1^2}\left[I_Y S_Z+I_Z S_Y,C_6\right]-\frac{i}{2}f_1(t)-\frac{1}{12}f_2(t),
\end{aligned} \tag{80}$$

The integration of the function $G_3(t)$

$$F_3=\frac{1}{T}\int_0^T G_3(\tau)\,\mathrm{d}\tau, \tag{81}$$

yield

$$F_3 = \frac{d^3}{64\omega_1^2}\left\{\left[I_Z S_Z + I_Y S_Y, \frac{C_1}{4} - \frac{C_4}{4} - 2C_5\right] + \left[I_Y S_Z + I_Z S_Y, C_6\right]\right\}. \quad (82)$$

A2. Cross-Polarization Description

In CP experiment, there is a strong coupling between a bath of ^{1}H and low-gamma nuclei, as shown in Figure 2. The mechanism of polarization transfers from ^{1}H to low-gamma nuclei, **X**, is presented in Figure 3.

The following Figure 3 is a basic succinct description of the Cross-Polarization experiment in solid-state NMR shown in Figure 2.

Let us consider two heteronuclear spins, I and S, that resonate at frequencies ω_I and ω_S such as,

$$\omega_I = \gamma_I B_0 \quad (83)$$

and

$$\omega_S = \gamma_S B_0 . \quad (84)$$

The coefficients γ_I and γ_S are the gyromagnetic ratios of spins I and S, respectively. B_0 is the external field, and B_{1i} (with $i = I, S$) is the respective

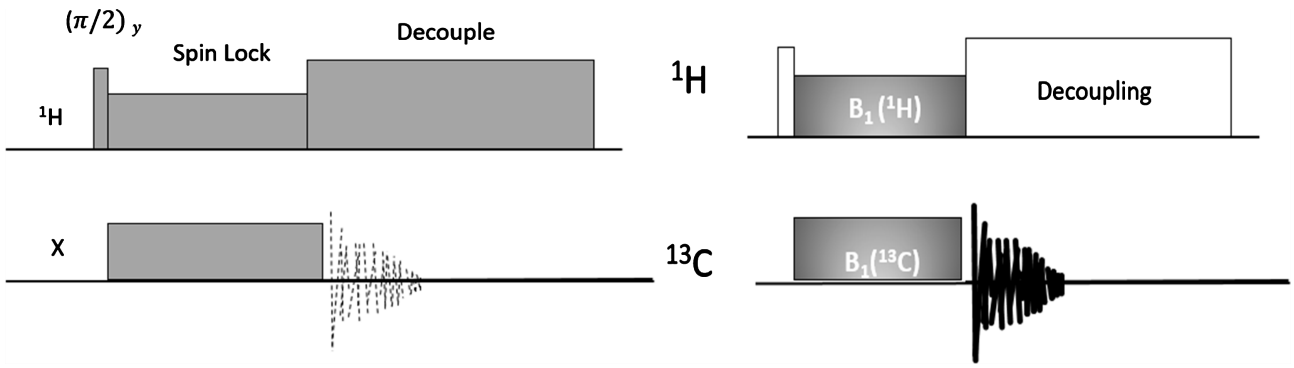

Figure 2. Polarization transfer from 1H to low gamma nuclei (X).

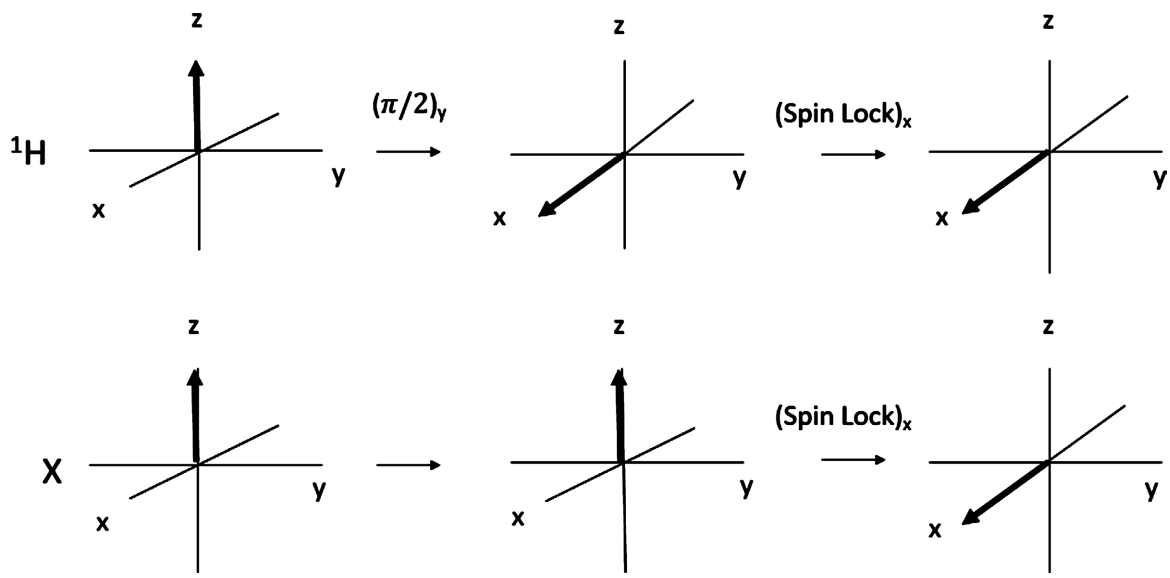

Figure 3. Basic description of CP experiment.

resonant field. The pulse sequences applied to I or S affect both heteronuclear spins. If the resonant fields are applied to I and S, each spin precesses with a frequency

$$\Omega_I = \gamma_I B_{1I} \tag{85}$$

and

$$\Omega_S = \gamma_S B_{1S} \tag{86}$$

The precession frequencies match by adjusting the resonant fields B_{1i} of individual nuclei. When these conditions match, we obtain the so-called Hartmann-Hahn condition [54] [57]:

$$\gamma_I B_{1I} = \gamma_S B_{1S}$$

As described in Figure 4, the classical description of CP uses the concept of spin temperature, which is valid as long as the system contains a large number of spins with strong ^{1}H-^{1}H dipolar couplings present [24] [33] [60]-[71].

During the cross polarization experiment shown in Figure 5, the abundant nucleus (typically, ^{1}H) and the observed nucleus (typically, ^{13}C) are spin-locked as shown in Figure 6 and Figure 7.

The spin-lock effect is similar to the Zeeman interaction in the sense that the effect gives rise to a splitting as shown in the Figure 8.

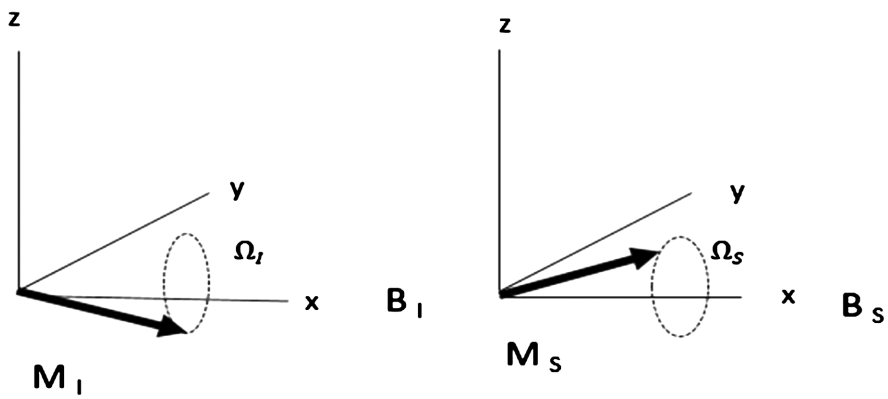

Figure 4. Precession of Resonant fields.

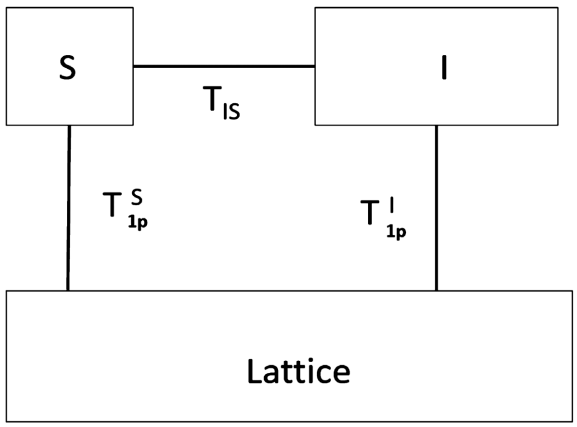

Figure 5. Classical description of CP.

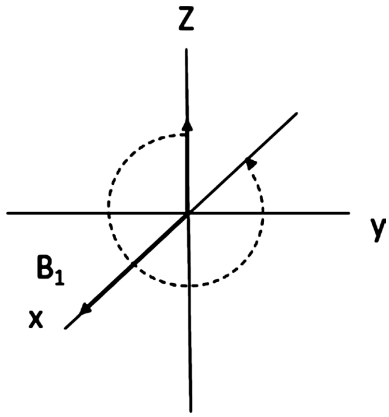

Figure 6. Pulse rotates spins.

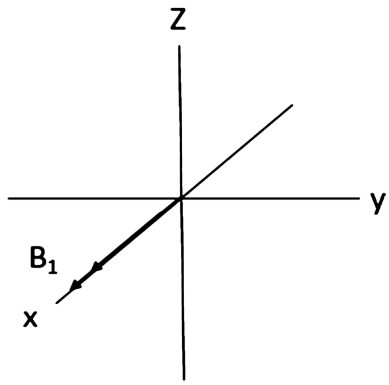

Figure 7. Spin-lock pulse trapping spins.

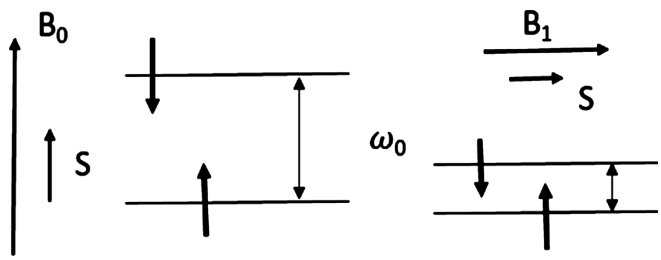

Figure 8. Similarity between the spin-lock effect and the Zeeman interaction.

When B_0, γ_H and γ_C are all fixed, the Zeeman splitting is different for ^{1}H and ^{13}C as illustrated in the Figure 9(a) and Figure 9(b), *i.e.*

$$\omega_0^H \neq \omega_0^C \tag{87}$$

where

$$\omega_0^H = \gamma_H B_0 \tag{88}$$

and

$$\omega_0^C = \gamma_C B_0 . \tag{89}$$

However, when the spin-lock fields are chosen appropriately, the splitting for ^{1}H and ^{13}C becomes identical, as illustrated in the Figure 10(a) and Figure 10(b) *i.e.*

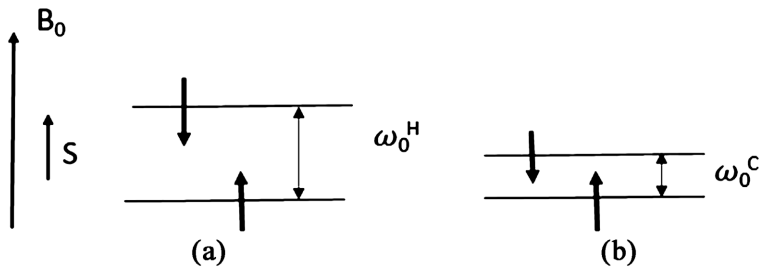

Figure 9. Zeeman splitting is different for ^{1}H and ^{13}C.

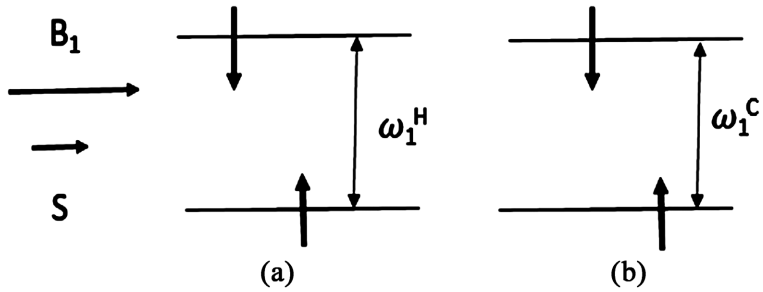

Figure 10. The spin-lock fields are chosen suitably.

$$\omega_1^H = \omega_1^C, \tag{90}$$

where

$$\omega_0^H = \gamma_H B_0 \tag{91}$$

and

$$\omega_0^C = \gamma_C B_0. \tag{92}$$