Published in final edited form as:

Solid State Nucl Magn Reson. 2012 February ; 41: 32–47. doi:10.1016/j.ssnmr.2011.11.004.

Efficient theory of dipolar recoupling in–solid state nuclear magnetic resonance of rotating solids using Floquet-Magnus expansion: Application on BABA and C7 radiofrequency pulse sequences

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Abstract

This article describes the use of an alternative expansion scheme called Floquet-Magnus expansion (FME) to study the dynamics of spin system in solid-state NMR. The main tool used to describe the effect of time-dependent interactions in NMR is the average Hamiltonian theory (AHT). However, some NMR experiments, such as sample rotation and pulse crafting, seem to be more conveniently described using the Floquet theory (FT). Here, we present the first report highlighting the basics of the Floquet-Magnus expansion (FME) scheme and hint at its application on recoupling sequences that excite more efficiently double-quantum coherences, namely BABA and C7 radiofrequency pulse sequences. The use of $A_n(t)$ functions available only in the FME scheme, allows the comparison of the efficiency of BABA and C7 sequences.

Keywords

Average Hamiltonian Theory; Floquet Theory; Floquet-Magnus Expansion; Magic Angle Spinning; BABA Pulse Sequence; C7 Pulse Sequence

I. INTRODUCTION

The power of solid-state NMR is based on its ability to elucidate molecular structure and dynamics in systems not amenable to characterization by other techniques. As such, solid-

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state NMR techniques have been applied to many studies such as determination of accurate intermolecular distances [1, 2] and molecular torsion angles [3, 4]. Several techniques to estimate these parameters make use of double-quantum coherence (DQC). For a spin system subject to magic-angle spinning (MAS), the spin Hamiltonian is the sum of the off-resonance, chemical shift anisotropy (CSA), J coupling, and dipolar interaction. In the present article, we ignore effects of the off-resonance, chemical shift anisotropy, and J couplings. We extend the description of the double-quantum (DQ) dynamics during dipolar recoupling beyond the first-order limit, which generally assumes chemical shift anisotropy effects negligible compared to large dipolar couplings. We only consider and use the dipole-dipole coupling to generate DQC. Generally, experiments with DQC allow for effective suppression of unwanted signals arising from naturally abundant nuclei, while leaving signals arising from coupled spin-pairs [5]. Important features of any DQC excitation technique are the excitation efficiency of DQC and the time scale on which the excitation occurs. Therefore, much effort is spent on the design of recoupling sequences that are able to produce DQC with high efficiency and on a short time scale. DQ recoupling is very useful in NMR spectroscopy, so success of this approach will require a solid understanding of the dynamics of recoupled multiple-spin systems. In this work, we apply a promising tool for studying spin dynamics, the Floquet-Magnus expansion (FME) developed by Casas et al. [6] and recently introduced to solid state NMR by Mananga et al. [7], to compare the performance of two important recoupling sequences (BABA and C7) [8, 9]. These sequences allow highly resolved DQ spectra to be obtained. To the best of our knowledge, this paper represents the first report of such type.

The FME approach is the combination of the two major methods used to describe the spin dynamics in solid-state NMR: the average Hamiltonian theory based on the Magnus expansion and the Floquet theory based on the Fourier expansion. The first method, AHT, was developed by Waugh and Haeberlen in 1968 [10] and is appropriate for stroboscopic sampling. However, the technique of AHT does not sufficiently describe the case of MAS [11, 12] spectra because in this case, the signal is usually observed continuously with a time resolution much shorter than the rotor period [13, 14, 15]. The second method, FT, developed by Vega [16] and Maricq [17], provides a more universal approach for the description of the full time dependence of the response of a periodically time-dependent system, but is most of the time impractical. However, the FT approach allows the computation of the full spinning sideband pattern that is of importance in many MAS experimental circumstances to obtain information on anisotropic sample properties. The FME approach can be used to solve a time-dependent linear differential equation which is a central problem in solid state NMR and in quantum physics in general. The FME scheme will be useful in the field of solid-state NMR to 1) shed new lights on the established AHT and FT; 2) greatly simplify the calculation of higher order terms and 3) provide a more intuitive understanding of spin dynamics processes.

In the following sections of this paper, we describe the Floquet-Magnus expansion and explicitly give the first contributions of the scheme with the addition of higher order effects (F_3 , $A_3(t)$) as an improvement to the first two orders (F_1 , $A_1(t)$) and (F_2 , $A_2(t)$). The FME scheme is then applied to BABA, BABA2 and C7 pulse sequences with the inclusion of

numerical analysis of the pulse sequences. A comparison of the efficiency of BABA, BABA2 and C7 sequences to produce DQ terms via the use of $A_1(t)$ and $A_2(t)$ functions is made. These operator functions facilitate the evaluation of the spin during or in between the RF pulses.

II. THEORY

II – A FLOQUET - MAGNUS EXPANSION (FME) DESCRIPTION

In the following, we use the FME approach to analyze the spin dynamics evolving under the dipolar interaction subject to two pulse sequences BABA, BABA2 and C7 shown respectively in Fig. 1, Fig. 2 and Fig. 3. These recoupling pulse sequences are known to be very efficient in exciting double-quantum coherences.

An illuminating approach for studying the dynamics of a spin system subject to a RF perturbation, given by the FME [6, 7, 19], can be to consider instead of the first and second order F_1 and F_2 that are identical to their counterparts in AHT and FT, but the $A_{1,2}(t)$ functions, available only in the FME scheme. This approach will be shown to provide a new way for evaluating the spin evolution during “the time in between” through the Magnus expansion of the operator connected to this part of the evolution. Using the Floquet theory [20, 21, 22], which is a branch of the theory of ordinary differential equations relating to the class of solutions of linear differential equations of the form

$$i\frac{dU}{dt}=H(t)U(t) \quad (1)$$

with initial condition

$$U(0)=I, \quad (2)$$

we can writing

$$U(t)=P(t)e^{-itF} \quad (3)$$

where $H(t)$, F and $P(t)$ are n by n matrices. $H(t)$ is a complex n by n matrix-valued function and its matrix elements are integrable periodic functions of time t with period denoted T . $P(t)$ is a periodic function of time with period T , i.e. $P(t) = P(t + T)$ and F is constant. In NMR, this structure is exploited in many situations including time-dependent periodic magnetic fields or sample spinning, which is the focus of this paper.

Using the exponential ansatz

$$P(t)=e^{-i\Lambda(t)} \text{ (with } \Lambda(t+T)=\Lambda(t)), \quad (4)$$

we approximate solutions in the following form of the propagator

$$U(t)=e^{i\Lambda(t)}e^{-itF}. \quad (5)$$

The function $\Lambda(t)$ provides an alternative way for evaluating the spin behavior in between the stroboscopic observation points, and F is the time independent Hamiltonian that governs the evolution of the propagator $U(t)$.

Considering the perturbation expansions for $\Lambda(t)$ and F

$$\Lambda(t)=\sum_{k=1}^{\infty}\Lambda_k(t), \quad (6)$$

$$F=\sum_{k=1}^{\infty}F_k \quad (7)$$

with

$$\Lambda_k(0)=0, \quad (8)$$

for all k , and following the procedure described in references [6] and [19], the above propagator Eq. (5) gives

$$U(t)=e^{-i\sum_{k=1}^{\infty}\Lambda_k(t)}e^{-it\sum_{k=1}^{\infty}F_k}. \quad (9)$$

Casas and al. [19] derived explicitly, the following equations,

$$\Lambda_1(t)=\int_0^t H(x)dx-tF_1 \quad (10)$$

$$F_1=\frac{1}{T}\int_0^T H(x)dx \quad (11)$$

$$\Lambda_2(t)=\frac{1}{2}\int_0^t [H(x)+F_1, \Lambda_1(x)]dx-tF_2 \quad (12)$$

$$F_2=\frac{1}{2T}\int_0^T [H(x)+F_1, \Lambda_1(x)]dx \quad (13)$$

The third order terms are also given in the appendix A0. Recently, we derived the general formula for the contribution of the Floquet-Magnus expansion [7] as following

$$\Lambda_n(t)=\int_0^t G_n(\tau)d\tau-tF_n+\Lambda_n(0) \quad (14)$$

$$F_n = \frac{1}{T} \int_0^T G_n(\tau) d\tau \quad (15)$$

where $G_n(\tau)$ functions are constructed using the FME recursive generation scheme [6, 19]. The first two orders explicit formula are:

$$\Lambda_1(t) = \Lambda_1(0) + \int_0^t G_1(\tau) d\tau - tF_1 \quad (16)$$

with

$$G_1(\tau) = H(\tau). \quad (17)$$

$$\Lambda_1(T) = \Lambda_1(0) \quad (18)$$

yields

$$F_1 = \frac{1}{T} \int_0^T H(\tau) d\tau \quad (19)$$

Second order terms are

$$\Lambda_2(t) = \int_0^t G_2(\tau) d\tau - tF_2 + \Lambda_2(0) \quad (20)$$

with

$$G_2(\tau) = -\frac{i}{2} [H(\tau) + F_1, \Lambda_1(\tau)]. \quad (21)$$

$$\Lambda_2(T) = \Lambda_2(0) \quad (22)$$

gives

$$F_2 = -\frac{i}{2T} \int_0^T [H(\tau) + F_1, \Lambda_1(\tau)] d\tau \quad (23)$$

$\Lambda_n(t)$ is the operator that describes the evolution within the period and $F_n(t)$ is the Hamiltonian governing the evolution at multiple periods. The two operators $\Lambda_n(t)$ and $F_n(t)$ are inter-dependent. While Floquet theory can also describe the time-evolution for arbitrary times, the FME approach however, can evaluate spin dynamics easier than FT and AHT. The additional terms $\Lambda_n(t)$ ($n = 1, 2, \dots$) in our general expressions [7] differ from the generally assumed $\Lambda_n(0) = 0$ [6]. However, in this article, we use the expressions of Casas and al. [6] as first-order contributions to the FME, where all $\Lambda_n(0)$ are assumed to be zero.

Note that, the FME scheme is not restricted to dipolar or quadrupolar interaction, and can be applied to any case.

For a spin system subject to MAS, the spin Hamiltonian is the sum of the off-resonance, chemical shift anisotropy, J coupling, and dipolar interaction. In the present article, we ignore off-resonance, chemical shift anisotropy, and J couplings. The analysis of the removal of the chemical shift interactions is the subject of a forthcoming paper [25]. In that work, we follow the explicit method described by Tycko for the removal of chemical shift interactions [24]. The current work however, is restricted to the study of dipolar interaction ($H_D(t)$), and the following substitution must be done in the above Eqs. (10) – (13),

$$H(t)=H_D(t). \quad (24)$$

The dipolar spin interaction MAS is given by

$$H_D(t)=\frac{1}{2}\sum_{i\neq j}\omega_D^{ij}(t)T_{20}^{ij} \quad (25)$$

where

$$T_{20}^{ij}=\frac{1}{\sqrt{6}}[2I_{zz}^{ij}-I_{xx}^{ij}-I_{yy}^{ij}] \quad (26)$$

and

$$\omega_D^{ij}(t)=b_{ij}\sum_{n=-2}^2C_n^{ij}(\alpha^{ij},\beta^{ij},\gamma^{ij})e^{-in\omega_R t}=b_{ij}\sum_{n=-2}^2C_n^{ij}(\alpha^{ij},\beta^{ij})e^{-in(\omega_R t+\gamma^{ij})} \quad (27)$$

In the following description, we are working only with the first two orders contribution terms of the FME. It can be shown that, for BABA and C7 recoupling sequences, the second order term is small compared to the first order term.

II – B APPLICATIONS

Here we applied the first contribution terms of the Floquet-Magnus expansion to the dipolar Hamiltonian when irradiated with the BABA [8] and sevenfold symmetric radiofrequency pulse sequences [9]. The degree to which these pulse sequences recouple magnetic dipolar between nuclear spins is useful for preparing and detecting double quantum coherence.

II – B – 1 APPLICATION OF THE FLOQUET - MAGNUS EXPANSION (FME) TO BABA PULSE SEQUENCE OF ONE ROTOR PERIOD (τ_R)

The broadband BABA pulse sequences shown in Fig.1 are built by suitable modification of the basic pulse sequence [8],

$$[(90_X^0 - \frac{\tau_R}{2} - 90_X^0)(90_Y^0 - \frac{\tau_R}{2} - 90_Y^0)],$$

where the 90° pulses in the middle of the pulse sequence and between different cycles are placed Back-to-Back (BABA). As shown below, the timing of the BABA sequence is important for full synchronization of the sample rotation, that is, for generating a pure DQ Hamiltonian. Using the FME, we are interested in calculating the degree to which the dipolar Hamiltonian leads to the maximum strength of the DQ Hamiltonian as a result of irradiating an ensemble of dipolar-coupled spin-pairs with the basic and the broadband BABA pulse sequence acting respectively on τ_R . In this paper, BABA pulse sequence acting on one rotor period τ_R is constructed from four rf pulses, with flip angles $\{\frac{\pi}{2}, \frac{\pi}{2}, \frac{\pi}{2}, \frac{\pi}{2}\}$ and rf phases $\{X, -X, Y, -Y\}$. The calculation begins with the definition of the dipolar spin interaction MAS Hamiltonian and using Eqs. (25), (26), and (27) where α, β and γ are Euler angles describing the orientation of a given molecule or crystallite in the MAS rotor. $b_{ij} = 3(\gamma)^2 \hbar/R^3_{ij}$ is the coupling constant, where γ is the gyromagnetic ratio for nuclear spins of type I and R_{ij} is the internuclear distance. The coefficients C_n^{ij} can be expressed as

$$C_n^{ij}(\alpha^{ij}, \beta^{ij}) = d_{0,n}^2(\theta_M) \sum_{n'=-2}^2 (-1)^{n'} Y_{2n'}^{ij} e^{-in\alpha^{ij}} d_{n-n'}^2(\beta^{ij}) \quad (28)$$

where $d_{nm}^2(\beta^{ij})$ are second-rank reduced Wigner rotation matrix elements, and θ_M is the magic angle, and $d_{00}^2(\theta_M) = 0, C_0^{ij} = 0$ [23]. Y_{2n}^{ij} and T_{2n}^{ij} are two independent types of rotations: Y_{2n}^{ij} is a basis for an irreducible representation of rotations of the spatial coordinates of the sample, and $\{Y_{2n}^{ij}\}$ are second-rank spherical harmonics; T_{2n}^{ij} is a basis for an irreducible representation of rotations of the spin angular momenta, and $\{T_{2n}^{ij}\}$ are second-rank irreducible tensor operators [24]. See appendix A3 for a more detailed description.

We can compute the toggling frame during each half of the rotor period. We have For :

$$0 \leq t < \frac{\tau_R}{2},$$

$$\begin{aligned} \tilde{H}_D(t) &= \frac{1}{2} \sum_{i \neq j} \omega_D^{ij}(t) R_X^+ \left(\frac{\pi}{2} T_{20}^{ij} R_X \left(\frac{\pi}{2} \right) \right. \\ &= \frac{1}{2} \sum_{i \neq j} \omega_D^{ij}(t) \frac{1}{\sqrt{6}} [2I_{YY}^{ij} - I_{XX}^{ij} - I_{ZZ}^{ij}] \quad (29) \\ &= \frac{1}{2} \sum_{i \neq j} \omega_D^{ij}(t) H_{YY}^{ij} \end{aligned}$$

where

$$H_{YY}^{ij} = \frac{1}{\sqrt{6}} [2I_{YY}^{ij} - I_{XX}^{ij} - I_{ZZ}^{ij}] \quad (30)$$

and for : $\frac{\tau_R}{2} \leq t < \tau_R$

$$\begin{aligned}
 \tilde{H}_D(t) &= \frac{1}{2} \sum_{i \neq j} \omega_D^{ij}(t) R_Y^+ \left(\frac{\pi}{2} T_{20}^{ij} R_Y \left(\frac{\pi}{2} \right) \right) \\
 &= \frac{1}{2} \sum_{i \neq j} \omega_D^{ij}(t) \frac{1}{\sqrt{6}} [2I_{XX}^{ij} - I_{ZZ}^{ij} - I_{YY}^{ij}] \quad (31) \\
 &= \frac{1}{2} \sum_{i \neq j} \omega_D^{ij}(t) H_{XX}^{ij}
 \end{aligned}$$

where

$$H_{XX}^{ij} = \frac{1}{\sqrt{6}} [2I_{XX}^{ij} - I_{ZZ}^{ij} - I_{YY}^{ij}] \quad (32)$$

Consider the BABA pulse sequence in the following representation

In this new picture, the toggling frame is written as

$$\tilde{H}_D(t) = H_{YY}(t)\theta_Y(t) + H_{XX}(t)\theta_X(t) \quad (33)$$

where

$$H_{\alpha\alpha}(t) = \frac{1}{2} \sum_{i \neq j} \omega_D^{ij}(t) H_{\alpha\alpha}^{ij}, \alpha = X, Y, Z. \quad (34)$$

The function $\theta(t)$ is represented as following

Eq. (33) is now written as

$$\tilde{H}_D(t) = H_{YY}(t)\theta(t) + H_{XX}(t)[1 - \theta(t)] \quad (35)$$

The time-dependent function $\theta(t)$ can be expressed in the form of the Fourier expansion,

$$\theta(t) = \sum_{n=-\infty}^{+\infty} a_n \exp(-in\omega_R t) \quad (36)$$

With a_n representing the time-independent Fourier coefficients corresponding to the Fourier index n . The coefficient a_k can be obtained

$$a_k = \frac{1}{\tau_R} \int_0^{\tau_R} \theta(t) e^{ik\omega_R t} dt \quad (37)$$

The coefficients in the first half of the sequence are the following

$$a_k^X = \frac{1}{\tau_R} \int_0^{\tau_R/2} e^{ik\omega_R t} dt \quad (38)$$

which are given explicitly by

$$a_o^X = \frac{1}{2}, \quad (39)$$

$$a_k^X = \frac{1}{2\pi ik} (e^{ik\pi} - 1). \quad (40)$$

In the second half of the sequence, they are

$$a_k^Y = \frac{1}{\tau_R} \int_{\tau_R/2}^{\tau_R} e^{ik\omega_R t} dt \quad (41)$$

which can also be written explicitly as

$$a_o^Y = \frac{1}{2}, \quad (42)$$

$$a_k^Y = \frac{1}{2\pi ik} (1 - e^{ik\pi}). \quad (43)$$

Globally, we have

$$a_o^X = a_o^Y = \frac{1}{2}, \quad (44)$$

$$a_k^X = -a_k^Y = a_k. \quad (45)$$

The toggling frame Eq. (35) is rewritten as

$$\begin{aligned} \tilde{H}_D(t) &= \frac{1}{2} \sum_{i \neq j} \omega_D^{ij}(t) \left(\sum_{n=-\infty}^{+\infty} a_n e^{-in(\omega_R t + \gamma^{ij})} \right) H_{YY}^{ij} + \\ &\quad \frac{1}{2} \sum_{i \neq j} \omega_D^{ij}(t) \left(1 - \sum_{n=-\infty}^{+\infty} a_n e^{-in(\omega_R t + \gamma^{ij})} \right) H_{XX}^{ij} \\ &= \frac{1}{2} \sum_{i \neq j} \omega_D^{ij}(t) \left(a_0 + \sum_{k \neq 0} a_k e^{-ik(\omega_R t + \gamma^{ij})} \right) H_{YY}^{ij} + \\ &\quad \frac{1}{2} \sum_{i \neq j} \omega_D^{ij}(t) \left(1 - a_0 - \sum_{k \neq 0} a_k e^{-ik(\omega_R t + \gamma^{ij})} \right) H_{XX}^{ij} \\ &= \frac{1}{2} \sum_{i \neq j} \omega_D^{ij}(t) a_0 (H_{XX}^{ij} + H_{YY}^{ij}) + \\ &\quad \frac{1}{2} \sum_{i \neq j} \omega_D^{ij}(t) \sum_{k \neq 0} a_k e^{-ik(\omega_R t + \gamma^{ij})} (H_{YY}^{ij} - H_{XX}^{ij}) \end{aligned} \quad (46)$$

Note that,

$$H_{XX}^{ij} + H_{YY}^{ij} = \frac{1}{\sqrt{6}} (I_{XX}^{ij} + I_{YY}^{ij} - 2I_{ZZ}^{ij}) \equiv \frac{1}{\sqrt{6}} H_{ZQ}^{ij}, \quad (47)$$

and

$$H_{YY}^{ij} - H_{XX}^{ij} = \frac{3}{\sqrt{6}} (I_{YY}^{ij} - I_{XX}^{ij}) \equiv \frac{3}{\sqrt{6}} H_{DQ}^{ij}. \quad (48)$$

Considering Eqs. (47) and (48), the Eq. (46) is written as

$$\begin{aligned} \tilde{H}_D(t) &= \frac{1}{2} \sum_{i \neq j} \omega_D^{ij}(t) a_0 \frac{1}{\sqrt{6}} (I_{XX}^{ij} + I_{YY}^{ij} - 2I_{ZZ}^{ij}) + \\ &\quad \frac{1}{2} \sum_{i \neq j} \omega_D^{ij}(t) \sum_{k \neq 0} a_k e^{-ik(\omega_R t + \gamma^{ij})} \frac{3}{\sqrt{6}} (I_{YY}^{ij} - I_{XX}^{ij}) \\ &= \tilde{H}_{ZQ,D}(t) + \tilde{H}_{DQ,D}(t) \end{aligned} \quad (49)$$

where $\tilde{H}_{ZQ,D}$ is the first term and $\tilde{H}_{DQ,D}$ is the second term of Eq. (49), i.e.

$$\tilde{H}_{DQ} = \frac{3}{2\sqrt{6}} \sum_{i \neq j} \omega_D^{ij}(t) \sum_{k \neq 0} a_k e^{-ik(\omega_R t + \gamma^{ij})} (I_{YY}^{ij} - I_{XX}^{ij}). \quad (50)$$

Substituting Eq. (27) into Eq. (50), we have

$$\begin{aligned} \tilde{H}_{DQ} &= \frac{3}{2\sqrt{6}} \sum_{i \neq j} b_{ij} \sum_{n=-2}^{+2} C_n^{ij} \sum_{k \neq 0} a_k e^{-ik(\omega_R t + \gamma^{ij})} e^{-in(\omega_R t + \gamma^{ij})} (I_{YY}^{ij} - I_{XX}^{ij}) \\ &= \frac{3}{2\sqrt{6}} \sum_{i \neq j} b_{ij} \sum_{n=-2}^{+2} C_n^{ij} \sum_{k \neq 0} a_k e^{-i(n+k)(\omega_R t + \gamma^{ij})} (I_{YY}^{ij} - I_{XX}^{ij}) \end{aligned} \quad (51)$$

Setting $n + k = m$, we have

$$\begin{aligned}\tilde{H}_{DQ} &= \frac{3}{2\sqrt{6}} \sum_{i \neq j} b_{ij} \sum_{n=-2}^{+2} C_n^{ij} \sum_{m=-\infty}^{+\infty} a_{m-n} e^{-im(\omega_R t + \gamma^{ij})} (I_{YY}^{ij} - I_{XX}^{ij}) \\ &= \frac{3}{2\sqrt{6}} \sum_{i \neq j} b_{ij} \sum_{m=-\infty}^{+\infty} e^{-im(\omega_R t + \gamma^{ij})} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij} (I_{YY}^{ij} - I_{XX}^{ij})\end{aligned}\quad (52)$$

This toggling Hamiltonian of the double quantum term can be split in two parts as following: the zero order term corresponding to $m = 0$, which is the average Hamiltonian theory, and the higher order terms.

$$\begin{aligned}\tilde{H}_{DQ} &= \frac{3}{2\sqrt{6}} \sum_{i \neq j} b_{ij} \sum_{n=-2}^{+2} a_{-n} C_n^{ij} (I_{YY}^{ij} - I_{XX}^{ij}) + \\ &\frac{3}{2\sqrt{6}} \sum_{i \neq j} b_{ij} \sum_{m=-\infty}^{+\infty} e^{-im(\omega_R t + \gamma^{ij})} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij} (I_{YY}^{ij} - I_{XX}^{ij})\end{aligned}\quad (53)$$

writing the Eq. (52) more explicitly lead to

$$\begin{aligned}\tilde{H}_{DQ} &= \underbrace{\left\{ \frac{3}{2\sqrt{6}} \sum_{i \neq j} b_{ij} \sum_{n=-2}^{+2} a_{-n} C_n^{ij} \right\}}_{AHT = \overline{\omega_D^{ij}}} (I_{YY}^{ij} - I_{XX}^{ij}) + \\ &\sum_{m=-\infty}^{+\infty} e^{im(\omega_R t + \gamma^{ij})} \underbrace{\left\{ \frac{3}{2\sqrt{6}} \sum_{i \neq j} b_{ij} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij} \right\}}_{\langle \omega_D^{ij} \rangle_m} (I_{YY}^{ij} - I_{XX}^{ij})\end{aligned}\quad (54)$$

Using Eqs. (39)–(45), we can write the following

$$a_{-n} = \frac{-1}{2\pi i n} (e^{-in\pi} - 1), \quad (55\text{-a})$$

$$a_{-1} = \frac{1}{\pi i}, \quad (55\text{-b})$$

$$a_1 = \frac{-1}{\pi i}, \quad (55\text{-c})$$

and

$$a_{-2} = a_2 = 0. \quad (55\text{-d})$$

A straightforward calculation gives the first order average Hamiltonian, which is also the first order contributions to the Floquet-Magnus expansion (Eq. (11)) $F_1 = \frac{1}{T} \int_0^T \tilde{H}_D(t) dt$, which is calculated by integrating over $[0, \tau_R]$ to obtain the following result

$$F_1 = \overline{H}^0 = \frac{3}{2i\sqrt{6}\pi} \sum_{i \neq j} b_{ij} (C_1^{ij} - C_{-1}^{ij}) (I_{YY}^{ij} - I_{XX}^{ij}) \quad (56)$$

Or more explicitly,

$$F_1 = \overline{H}^0 = \frac{3}{2i\sqrt{6}\pi} \sum_{i \neq j} b_{ij} [C_1^{ij}(\alpha^{ij}, \beta^{ij}) e^{-i\gamma^{ij}} - C_{-1}^{ij}(\alpha^{ij}, \beta^{ij}) e^{+i\gamma^{ij}}] (I_{YY}^{ij} - I_{XX}^{ij}) \quad (57)$$

We note that

$$T_{22}^{ij} + T_{2-2}^{ij} = I_{XX}^{ij} - I_{YY}^{ij}, \quad (58)$$

and

$$\sin \gamma^{ij} = \frac{e^{i\gamma^{ij}} - e^{-i\gamma^{ij}}}{2i} \quad (59)$$

The constants $C_1^{ij}(\alpha^{ij}, \beta^{ij})$ and $C_{-1}^{ij}(\alpha^{ij}, \beta^{ij})$ are derived in Appendix A3. Considering only the central term in Eq. (172), we have

$$C_1^{ij}(\alpha^{ij}, \beta^{ij}) = \frac{1}{\sqrt{3}} Y_{20} e^{-i\alpha^{ij}} d_{10}^2(\beta^{ij}) = Y_{20} e^{-i\alpha^{ij}} \frac{1}{\sqrt{3}} (-1) \sqrt{\frac{3}{2}} \sin \beta^{ij} \cos \beta^{ij} = \frac{-1}{2\sqrt{2}} Y_{20} e^{-i\alpha^{ij}} \sin 2\beta^{ij} \quad (60)$$

where the Wigner d-matrix elements with swapper lower indices found with the relation

$$d_{nm}^j = (-1)^{m-n} d_{mn}^j \quad (61)$$

has been used. In a similar vein, the constant $C_{-1}^{ij}(\alpha^{ij}, \beta^{ij})$ can also be derived. If Eqs. (58) and (59) are substituted into Eq. (57), we obtained the direct comparison between Eq. (57) and the zero-order average Hamiltonian of the dipolar Hamiltonian calculated by Feike et al. [8]

$$\overline{H}_D^0 = H_{DQ} = \frac{3}{\pi\sqrt{2}} \sum_{i>j} D^{ij} \sin(2\beta^{ij}) \sin(\gamma^{ij}) (T_{22}^{ij} + T_{2-2}^{ij}) \quad (62)$$

Therefore, the first order F_1 to the Floquet-Magnus expansion appears to be equivalent to the zero-order average Hamiltonian. Next, Eq. (10) can be computed as follows

$$\begin{aligned} \Lambda_1(t) &= \int_0^t \tilde{H}_D(t') dt' - t F_1 = \int_0^t \tilde{H}_{ZQ,D}(t') dt' + \int_0^t \tilde{H}_{DQ}(t') dt' - t F_1 \\ &= \int_0^t \tilde{H}_{ZQ,D}(t') dt' + \int_0^t \tilde{H}_{AHT^{(0)}}(t') dt' + \int_0^t \tilde{H}_{AHT^{(m)}}(t') dt' - t F_1 \quad (63) \\ &= \int_0^t \tilde{H}_{ZQ,D}(t) dt + \int_0^t \tilde{H}_{AHT^{(m)}}(t) dt \end{aligned}$$

which leads to

$$\begin{aligned}
\Lambda_1(t) = & \frac{1}{4\sqrt{6}} \sum_{i \neq j} b_{ij} [C_{-2}^{ij}(\alpha^{ij}, \beta^{ij}) e^{2i\gamma^{ij}} (\frac{1}{2i\omega_R})(e^{2i\omega_R t} - 1)] (I_{XX}^{ij} + I_{YY}^{ij} - 2I_{ZZ}^{ij}) + \\
& + \frac{1}{4\sqrt{6}} \sum_{i \neq j} b_{ij} [-C_2^{ij}(\alpha^{ij}, \beta^{ij}) e^{-2i\gamma^{ij}} (\frac{1}{2i\omega_R})(e^{-2i\omega_R t} - 1)] (I_{XX}^{ij} + I_{YY}^{ij} - 2I_{ZZ}^{ij}) \\
& + \frac{1}{4\sqrt{6}} \sum_{i \neq j} b_{ij} [-C_1^{ij}(\alpha^{ij}, \beta^{ij}) e^{-i\gamma^{ij}} (\frac{1}{i\omega_R})(e^{-i\omega_R t} - 1) + \\
& C_{-1}^{ij}(\alpha^{ij}, \beta^{ij}) e^{i\gamma^{ij}} (\frac{1}{i\omega_R})(e^{i\omega_R t} - 1)] (I_{XX}^{ij} + I_{YY}^{ij} - 2I_{ZZ}^{ij}) \\
& - \sum_{m=-\infty}^{+\infty} \frac{1}{im\omega_R} (e^{-im\omega_R t} - 1) [\frac{3}{2\sqrt{6}} \sum_{i \neq j} b_{ij} e^{-im\gamma^{ij}} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij}] (I_{YY}^{ij} - I_{XX}^{ij})
\end{aligned} \quad (64)$$

Next, we can calculate the second order terms due to the contributions of the Floquet-Magnus expansion by using Eq. (13). If we write the following

$$\tilde{H}_D(t) + F_1 = H_Z H_{ZQ}^{ij} + (H^0 + H^m) H_{DQ}^{ij} + H^0 H_{DQ}^{ij} \quad (65)$$

and

$$\Lambda_1(t) = A H_{ZQ}^{ij} + B H_{DQ}^{ij} \quad (66)$$

where the constants are

$$H_Z = \frac{1}{2} \sum_{i \neq j} \omega_D^{ij}(t) a_0 \frac{1}{\sqrt{6}}, \quad (67)$$

$$H^0 = \frac{3}{2\sqrt{6}} \sum_{i \neq j} b_{ij} \sum_{n=-2}^{+2} a_{-n} C_n^{ij}, \quad (68)$$

$$H^m = \sum_{m=-\infty}^{+\infty} e^{-im(\omega_R t + \gamma^{ij})} [\frac{3}{2\sqrt{6}} \sum_{i \neq j} b_{ij} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij}], \quad (69)$$

$$\begin{aligned}
A = & \frac{1}{4\sqrt{6}} \sum_{i \neq j} \left[C_{-2}^{ij}(\alpha^{ij}, \beta^{ij}) e^{2i\gamma^{ij}} (\frac{1}{2i\omega_R})(e^{2i\omega_R t} - 1) \right] + \\
& \frac{1}{4\sqrt{6}} \sum_{i \neq j} [-C_2^{ij}(\alpha^{ij}, \beta^{ij}) e^{-2i\gamma^{ij}} (\frac{1}{2i\omega_R})(e^{-2i\omega_R t} - 1)] \\
& + \frac{1}{4\sqrt{6}} \sum_{i \neq j} [-C_1^{ij}(\alpha^{ij}, \beta^{ij}) e^{-i\gamma^{ij}} (\frac{1}{i\omega_R})(e^{-i\omega_R t} - 1) + C_{-1}^{ij}(\alpha^{ij}, \beta^{ij}) e^{i\gamma^{ij}} (\frac{1}{i\omega_R})(e^{i\omega_R t} - 1)]
\end{aligned} \quad (70)$$

$$B = - \sum_{m=-\infty}^{+\infty} \frac{1}{im\omega_R} (e^{-im\omega_R t} - 1) [\frac{3}{2\sqrt{6}} \sum_{i \neq j} b_{ij} e^{-im\gamma^{ij}} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij}]. \quad (71)$$

Eq. (13) leads to

$$\begin{aligned}
F_2 = & \frac{1}{2T} \int_0^T [\tilde{H}_D(t') + F_1, \Lambda_1(t')] dt' \\
= & \frac{1}{2T} [\int_0^T H_Z B dt' - \int_0^T (2H^0 + H^m) A dt'] [H_{ZQ}^{ij}, H_{DQ}^{ij}] \\
= & \frac{1}{2T} [\int_0^T H_Z B dt' - \int_0^T (2H^0 + H^m) A dt'] [2(I_{XX}^{ij}, I_{YY}^{ij}) - 2(I_{XX}^{ij}, I_{ZZ}^{ij}) + 2(I_{YY}^{ij}, I_{ZZ}^{ij})]
\end{aligned} \quad (72)$$

The computation of each term of the above integral (see appendix A1) gives

$$\int_0^T H_z B dt = 0, \quad (73)$$

$$\int_0^T H^m A dt = 0, \quad (74)$$

$$2 \int_0^T H^0 A dt = 2 H^0 \int_0^{\tau_R} A dt, \quad (75)$$

$$\begin{aligned} \int_0^{\tau_R} A dt = & \frac{1}{4\sqrt{6}} \sum_{i \neq j} \left[C_{-2}^{ij} (\alpha^{ij}, \beta^{ij}) e^{2i\gamma^{ij}} \left(\frac{1}{2i\omega_R} \right) (-\tau_R) \right] + \\ & \frac{1}{4\sqrt{6}} \sum_{i \neq j} \left[-C_2^{ij} (\alpha^{ij}, \beta^{ij}) e^{-2i\gamma^{ij}} \left(\frac{1}{2i\omega_R} \right) (-\tau_R) \right] \\ & + \frac{1}{4\sqrt{6}} \sum_{i \neq j} \left[-C_1^{ij} (\alpha^{ij}, \beta^{ij}) e^{-i\gamma^{ij}} \left(\frac{1}{i\omega_R} \right) (-\tau_R) + C_{-1}^{ij} (\alpha^{ij}, \beta^{ij}) e^{i\gamma^{ij}} \left(\frac{1}{i\omega_R} \right) (-\tau_R) \right] \end{aligned} \quad (76)$$

Substituting Eqs. (73) - (76) into Eq. (72), we obtain

$$\begin{aligned} F_2 = & \frac{3}{2\sqrt{6}} \sum_{i \neq j} b_{ij} \sum_{n=-2}^{+2} a_{-n} C_n^{ij} \frac{1}{4\sqrt{6}} \left[C_{-2}^{ij} (\alpha^{ij}, \beta^{ij}) e^{2i\gamma^{ij}} \left(\frac{1}{2i\omega_R} \right) - C_2^{ij} (\alpha^{ij}, \beta^{ij}) e^{-2i\gamma^{ij}} \left(\frac{1}{2i\omega_R} \right) \right] * \\ & * [H_{zQ}^{ij}, H_{DQ}^{ij}] \\ & + \frac{3}{2\sqrt{6}} \sum_{i \neq j} b_{ij} \sum_{n=-2}^{+2} a_{-n} C_n^{ij} \frac{1}{4\sqrt{6}} \left[-C_1^{ij} (\alpha^{ij}, \beta^{ij}) e^{-i\gamma^{ij}} \left(\frac{1}{i\omega_R} \right) + C_{-1}^{ij} (\alpha^{ij}, \beta^{ij}) e^{i\gamma^{ij}} \left(\frac{1}{i\omega_R} \right) \right] * \\ & * [H_{zQ}^{ij}, H_{DQ}^{ij}] \end{aligned} \quad (77)$$

or more explicitly,

$$\begin{aligned} F_2 = & \frac{-\tau_R}{64\pi^2} \sum_{i \neq j} b_{ij} (C_1^{ij} - C_{-1}^{ij}) [C_{-2}^{ij} (\alpha^{ij}, \beta^{ij}) e^{2i\gamma^{ij}} - C_2^{ij} (\alpha^{ij}, \beta^{ij}) e^{-2i\gamma^{ij}}] [H_{zQ}^{ij}, H_{DQ}^{ij}] \\ & - \frac{\tau_R}{32\pi^2} \sum_{i \neq j} b_{ij} (C_1^{ij} - C_{-1}^{ij}) [-C_1^{ij} (\alpha^{ij}, \beta^{ij}) e^{2i\gamma^{ij}} + C_{-1}^{ij} (\alpha^{ij}, \beta^{ij}) e^{-2i\gamma^{ij}}] [H_{zQ}^{ij}, H_{DQ}^{ij}] \end{aligned} \quad (78)$$

Similarly, using Eq. (12), we can compute the second order terms $\Lambda_2(t)$ due to the contributions of the Floquet-Magnus expansion. We have

$$\Lambda_2(t) = \frac{1}{2} \left[\int_0^t H_z B dt' - \int_0^t (2H^0 + H^m) A dt' \right] [H_{zQ}^{ij}, H_{DQ}^{ij}] - t F_2 + \Lambda_2(0) \quad (79)$$

After calculations (see Appendix A1) we obtain

$$\begin{aligned}
\Lambda_2(t) = & \left[\frac{-1}{32\omega_R^2} \sum_{i \neq j} \left(b_{ij} \sum_{n=-2}^2 C_n^{ij} \right) \left(- \sum_{m=-\infty}^{+\infty} \frac{1}{m} \left[\sum_{i \neq j} b_{ij} e^{-im\gamma^{ij}} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij} \right] \right) \right] * \\
& * \left[\frac{1}{(n+m)} \right] [H_{ZQ}^{ij}, H_{DQ}^{ij}] \\
& + \left[\frac{-1}{32\omega_R^2} \sum_{i \neq j} \left(b_{ij} \sum_{n=-2}^2 C_n^{ij} \right) \left(- \sum_{m=-\infty}^{+\infty} \frac{1}{m} \left[\sum_{i \neq j} b_{ij} e^{-im\gamma^{ij}} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij} \right] \right) \right] * \\
& * \left[\frac{-1}{(n+m)} e^{-(n+m)i\omega_R t} \right] [H_{ZQ}^{ij}, H_{DQ}^{ij}] \\
& + \left[\frac{-1}{32\omega_R^2} \sum_{i \neq j} \left(b_{ij} \sum_{n=-2}^2 C_n^{ij} \right) \left(- \sum_{m=-\infty}^{+\infty} \frac{1}{m} \left[\sum_{i \neq j} b_{ij} e^{-im\gamma^{ij}} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij} \right] \right) \right] * \\
& * \left[\frac{1}{n} (e^{-in\omega_R t} - 1) \right] [H_{ZQ}^{ij}, H_{DQ}^{ij}] \\
& + \frac{1}{16\pi i \omega^2} \sum_{i \neq j} b_{ij} (C_1^{ij} - C_{-1}^{ij}) \left[\sum_{i \neq j} \frac{1}{4} C_{-2}^{ij} e^{2i\gamma^{ij}} (e^{2i\omega_R t} - 1) + \sum_{i \neq j} \frac{1}{4} C_2^{ij} e^{-2i\gamma^{ij}} (e^{-2i\omega_R t} - 1) \right] * \\
& * [H_{ZQ}^{ij}, H_{DQ}^{ij}] \\
& + \frac{1}{16\pi i \omega^2} \sum_{i \neq j} b_{ij} (C_1^{ij} - C_{-1}^{ij}) \left[\sum_{i \neq j} C_1^{ij} e^{-i\gamma^{ij}} (e^{-i\omega_R t} - 1) + \sum_{i \neq j} C_{-1}^{ij} e^{i\gamma^{ij}} (e^{i\omega_R t} - 1) \right] * \\
& * [H_{ZQ}^{ij}, H_{DQ}^{ij}] \\
& + \frac{1}{64\omega_R^2} \sum_{m=-\infty}^{+\infty} e^{-im\gamma^{ij}} \sum_{i \neq j} b_{ij} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij} \left[C_{-2}^{ij} e^{2i\gamma^{ij}} - C_2^{ij} e^{-2i\gamma^{ij}} - C_1^{ij} e^{-i\gamma^{ij}} + C_{-1}^{ij} e^{i\gamma^{ij}} \right] * \\
& * \left[\frac{e^{(2-m)i\omega_R t}}{(2-m)} \right] [H_{ZQ}^{ij}, H_{DQ}^{ij}] \\
& + \frac{1}{64\omega_R^2} \sum_{m=-\infty}^{+\infty} e^{-im\gamma^{ij}} \sum_{i \neq j} b_{ij} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij} \left[C_{-2}^{ij} e^{2i\gamma^{ij}} - C_2^{ij} e^{-2i\gamma^{ij}} - C_1^{ij} e^{-i\gamma^{ij}} + C_{-1}^{ij} e^{i\gamma^{ij}} \right] * \\
& * \left[\frac{-1}{(2-m)} \right] [H_{ZQ}^{ij}, H_{DQ}^{ij}] \\
& + \frac{1}{64\omega_R^2} \sum_{m=-\infty}^{+\infty} e^{-im\gamma^{ij}} \sum_{i \neq j} b_{ij} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij} \left[C_{-2}^{ij} e^{2i\gamma^{ij}} - C_2^{ij} e^{-2i\gamma^{ij}} - C_1^{ij} e^{-i\gamma^{ij}} + C_{-1}^{ij} e^{i\gamma^{ij}} \right] * \\
& * \left[\frac{(e^{-im\omega_R t} - 1)}{m} \right] [H_{ZQ}^{ij}, H_{DQ}^{ij}] + \Lambda_2(0) \\
& m \neq 0, m \neq 2, m \neq -n
\end{aligned} \tag{80}$$

NUMERICAL ANALYSIS OF BABA—For $m = 1$, consider a system of 2 spins. Only DQ terms are considered for the functions $\Lambda_1(t)$ and $\Lambda_2(t)$. We consider the simple case where the rotations are: $\alpha^{ij} = \beta^{ij} = \gamma^{ij} = 0$. The coefficients C_n^{ij} are

$C_1 = \frac{-1}{\sqrt{3}} \sin\Theta \cos\Theta e^{-i\Phi}$, $C_{-1} = 0$, $C_2 = \frac{1}{2\sqrt{6}} \sin^2\Theta e^{-2i\Phi}$ and $C_{-2} = 0$. For example, with $\Theta = \frac{\pi}{4}$ and $\Phi = 0$, the coefficients are $C_1 = \frac{-1}{2\sqrt{3}}$ and $C_2 = \frac{1}{4\sqrt{6}}$. The functions $\Lambda_1(t)$ and $\Lambda_2(t)$ are:

$$\Lambda_1(t) = \frac{1}{8\sqrt{2}\omega_R} \left(i - \frac{1}{\pi\sqrt{2}} \right) (e^{-i\omega_R t} - 1) (I_{YY}^{ij} - I_{XX}^{ij}) + \Lambda_1(0) \text{ and} \tag{81}$$

$$\begin{aligned}
\Lambda_2(t) = & \left\{ \frac{1}{768} \left[\frac{-1}{2} (e^{-2i\omega_R t} - 1) + (e^{-i\omega_R t} - 1) \right] + \right. \\
& \left. \frac{i}{192\pi\omega_R^2} \left[\frac{1}{8\sqrt{2}} (e^{-2i\omega_R t} - 1) - (e^{-i\omega_R t} - 1) \right] \right\} (I_{YY}^{ij} - I_{XX}^{ij}) \\
& - \left\{ \frac{1}{1536\omega_R^2} \left(1 - \frac{1}{2\sqrt{2}} \right) (e^{i\omega_R t} + e^{-i\omega_R t} - 2) \right\} (I_{YY}^{ij} - I_{XX}^{ij}) + \Lambda_2(0)
\end{aligned} \tag{82}$$

or writing these functions in terms of the rotor period, we have

$$\frac{\Lambda_1(t)}{b_{ij}\tau_R} = BABA_1(\phi) = \frac{1}{16\sqrt{2}\pi} \left(i - \frac{1}{\pi\sqrt{2}} \right) (e^{-i2\pi\phi} - 1) (I_{YY}^{ij} - I_{XX}^{ij}) \quad (83)$$

$$\begin{aligned} \frac{\Lambda_2(t)}{b_{ij}^2\tau_R^2} = BABA_2(\phi) = & \left\{ \frac{1}{768} \left[\frac{1}{2} (e^{-4\pi i\phi} - 1) + (e^{-i2\pi\phi} - 1) \right] + \right. \\ & \frac{i}{768\pi^3} \left[\frac{1}{8\sqrt{2}} (e^{-i4\pi\phi} - 1) - (e^{-i2\pi\phi} - 1) \right] \} (I_{YY}^{ij} - I_{XX}^{ij}) \\ & - \left\{ \frac{1}{6144\pi^2} \left(1 - \frac{1}{2\sqrt{2}} \right) (e^{i2\pi\phi} + e^{-i2\pi\phi} - 2) \right\} (I_{YY}^{ij} - I_{XX}^{ij}) \end{aligned} \quad (84)$$

where the variable is chosen to be a dimensionless number $\phi = \frac{t}{\tau_R}$. BABA functions (real, imaginary and absolute parts) are plot versus the dimensionless number ϕ .

Analysis of the figures: The plots of Fig. 4a and 4b respectively show the dimensionless functions Λ_1 and Λ_2 for BABA pulse sequence versus the dimensionless number ϕ . Fig. 4c shows the plot of both functions $\Lambda_1(t)$ and $\Lambda_2(t)$ versus ϕ . Due to the complexity of these functions ($\Lambda_1(t)$ and $\Lambda_2(t)$), real, imaginary, and absolute parts are plotted separately as function of ϕ . These functions depend on the DQ terms. Therefore, the study of the amplitude of DQ terms can be considered as a viable approach for controlling the complex spin dynamics of a spin system evolving under the dipolar interaction of BABA pulse sequence. The plot can be considered as a quantitative representation of the amplitude of the DQ coherence as a function of ϕ . The size of $BABA_1(\phi) = \frac{\Lambda_1(t)}{b_{ij}\tau_R}$ determine the amplitude of the DQ coherence, which indicates the degree of efficiency of the scheme. Figs. 4a, 4b, and 4c show respectively, the graphs of the functions $\frac{\Lambda_1(t)}{b_{ij}\tau_R} = BABA_1(\phi)$, $\frac{\Lambda_2(t)}{b_{ij}^2\tau_R^2} = BABA_2(\phi)$ and $(BABA_1(\phi), BABA_2(\phi))$ as a function of $\phi = \frac{t}{\tau_R}$. A closer look at Fig. 3c shows that the magnitude of $BABA_2(\phi)$ is small comparatively to the magnitude of $BABA_1(\phi)$, i.e.

$\left| \frac{\Lambda_2(t)}{b_{ij}^2\tau_R^2} \right| < \left| \frac{\Lambda_1(t)}{b_{ij}\tau_R} \right|$ as expected. As a result, $\Lambda_2(t)$ will be less useful in many cases. We can also observe that all graphs are strictly monotonous. This tells us that, the strength of the DQ terms increase continuously with time and no decoupling conditions occur in the BABA pulse sequence.

II – B – 2 BROADBAND BABA2 ACTING ON MULTIPLE OF TWO ROTOR PERIODS ($2\tau_R$)

In this article, the broadband BABA2 pulse sequence [8] acting on multiple of two rotor periods $2\tau_R$ is constructed from eighth rf pulses, with flip angles $\{\frac{\pi}{2}, \frac{\pi}{2}, \dots, \frac{\pi}{2}\}$ and rf phases $\{X, -X, Y, -Y, -X, X, -Y, Y\}$. Consider the BABA2 pulse sequence in the following representation

As described previously for BABA, the toggling frame in this new scheme is written similarly as in Eq. (33), in the following form

$$\tilde{H}_D(t) = H_{YY}(t)\theta_{YY}(t) + H_{XX}(t)\theta_{XX}(t) \quad (85)$$

$$\text{with } H_{\alpha\alpha}(t) = \frac{1}{2} \sum_{i \neq j} \omega_D^{ij}(t) H_{\alpha\alpha}^{ij} \text{ as before.} \quad (34)$$

The function $\theta(t)$ is represented as follows

(86)

(87)

Substituting Eqs. (86) and (87) into Eq. (85), we have the following

$$\tilde{H}_D(t) = H_{YY}(t)\theta_Y^2(t) + H_{XX}(t)\theta_X^2(t) = H_{YY}(t)\theta^2 + H_{XX}(t)(1 - \theta)^2 \quad (88)$$

The Fourier coefficients of the time-dependent function $\theta(t)$ expressed in Eq. (36) are now

$$a_k = \frac{1}{2\tau_R} \int_0^{2\tau_R} \theta(t) e^{ik\omega_R t} dt \quad (89)$$

The Fourier coefficients a_k^X in the “X-direction” of the above picture are computed as following

$$a_k^X = \frac{1}{2\tau_R} \left[\int_0^{\tau_R/2} e^{ik\omega_R t} dt + \int_{\tau_R}^{3\tau_R/2} e^{ik\omega_R t} dt \right] \quad (90-a)$$

and

$$a_0^X = \frac{1}{2\tau_R} \left[\int_0^{\tau_R/2} dt + \int_{\tau_R}^{3\tau_R/2} dt \right] \quad (90-b)$$

which give

$$a_k^X = \frac{1}{ik2\pi} [e^{ik\pi/2} - 1 + e^{-ik\pi/2} - e^{ik\pi}] \quad (91-a)$$

and

$$a_o^X = \frac{1}{2} \quad (91-b)$$

Similarly, in the “Y-direction” of the above picture, the Fourier coefficients a_k^Y are computed as follows

$$a_k^Y = \frac{1}{2\tau_R} [\int_{\tau_R/2}^{\tau_R} e^{ik\omega_R t} dt + \int_{3\tau_R/2}^{2\tau_R} e^{ik\omega_R t} dt] \quad (92-a)$$

and

$$a_0^Y = \frac{1}{2\tau_R} [\int_{\tau_R/2}^{\tau_R} dt + \int_{3\tau_R/2}^{2\tau_R} dt] \quad (92-b)$$

which give

$$a_k^Y = \frac{1}{ik2\pi} [e^{ik\pi} - e^{-ik\pi/2} + 1 - e^{ik\pi/2}] \quad (93-a)$$

and

$$a_o^Y = \frac{1}{2} \quad (93-b)$$

Finally, the following result is obtained

$$a_o^X = a_o^Y = a_0 = \frac{1}{2} \quad (94-a)$$

and

$$a_k^X = -a_k^Y = a_k \quad (94-b)$$

The toggling frame Eq. (88) can be evaluated as follow

$$\tilde{H}_D(t) = \frac{1}{2} \sum_{i \neq j} \omega_D^{ij}(t) \left(\sum_n a_n e^{-in(\omega_R t + \gamma^{ij})} \right)^2 H_{YY}^{ij} + \frac{1}{2} \sum_{i \neq j} \omega_D^{ij}(t) (1 - \sum_n a_n e^{-in(\omega_R t + \gamma^{ij})})^2 H_{XX}^{ij} \quad (95)$$

and substituting Eqs. (91), (93) and (94) into (95), we have

$$\begin{aligned} \tilde{H}_D(t) &= \frac{1}{2} \sum_{i \neq j} \omega_D^{ij}(t) \left(a_0 + \sum_{k \neq 0} a_k e^{-ik(\omega_R t + \gamma^{ij})} \right)^2 H_{YY}^{ij} + \\ &\quad \frac{1}{2} \sum_{i \neq j} \omega_D^{ij}(t) (1 - a_0 - \sum_{k \neq 0} a_k e^{-ik(\omega_R t + \gamma^{ij})})^2 H_{XX}^{ij} \\ &= \frac{1}{2} \sum_{i \neq j} \omega_D^{ij}(t) \left[a_0^2 + \left(\sum_{k \neq 0} a_k e^{-ik(\omega_R t + \gamma^{ij})} \right)^2 \right] (H_{XX}^{ij} + H_{YY}^{ij}) + \\ &\quad \frac{1}{2} \sum_{i \neq j} \omega_D^{ij}(t) 2a_0 \sum_{k \neq 0} a_k e^{-ik(\omega_R t + \gamma^{ij})} (H_{YY}^{ij} - H_{XX}^{ij}) \\ &= \tilde{H}_{ZQ,D}(t) + \tilde{H}_{DQ,D}(t) \end{aligned} \quad (96)$$

Similar results than Eqs. (55) and (55-a, b, c) are obtained for the double-quantum toggling Hamiltonian, but with change of coefficients in the AHT term as following

$$\begin{aligned} \tilde{H}_{DQ} &= \underbrace{\left\{ \frac{3}{2\sqrt{6}} \sum_{i \neq j} b_{ij} \sum_{n=-2}^{+2} a_{-n} C_n^{ij} \right\}}_{\{AHT=\omega_D^{ij}\}} (I_{YY}^{ij} - I_{XX}^{ij}) + \\ &\quad + \sum_{m=-\infty}^{+\infty} e^{-im(\omega_R t + \gamma^{ij})} \underbrace{\left\{ \frac{3}{2\sqrt{6}} \sum_{i \neq j} b_{ij} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij} \right\}}_{\{<\omega_D^{ij}>m\}} (I_{YY}^{ij} - I_{XX}^{ij}) \end{aligned} \quad (97)$$

From Eqs. (91) and (94), we have

$$a_k = \frac{1}{ik\pi} \left[\cos\left(k\frac{\pi}{2}\right) - \frac{1}{2}(1 + e^{ik\pi}) \right] \quad (98)$$

which can also be written as

$$a_{-n} = \frac{-1}{in\pi} \left[\cos\left(n\frac{\pi}{2}\right) - \frac{1}{2}(1 + e^{-in\pi}) \right] \quad (99)$$

and evaluated numerically

$$a_{-2} = \frac{1}{\pi i}, \quad (100-a)$$

$$a_2 = \frac{-1}{\pi i}, \quad (100-b)$$

and

$$a_{-1}=a_1=0. \quad (100-c)$$

Therefore, the first order contribution to the Floquet-Magnus expansion F_1 gives

$$F_1 = \bar{H}^0 = \frac{3}{2i\sqrt{6}\pi} \sum_{i \neq j} b_{ij} [C_2^{ij}(\alpha^{ij}, \beta^{ij}) e^{-2i\gamma^{ij}} - C_{-2}^{ij}(\alpha^{ij}, \beta^{ij}) e^{+2i\gamma^{ij}}] (I_{YY}^{ij} - I_{XX}^{ij}) \quad (101)$$

The constants $C_2^{ij}(\alpha^{ij}, \beta^{ij})$ and $C_{-2}^{ij}(\alpha^{ij}, \beta^{ij})$ are given by the Eq. (173). $\Lambda_1(t)$ is computed by using Eq. (10) and the result is similar to the solution of BABA (Eq. 64) by substituting coefficients $C_1^{ij}(\alpha^{ij}, \beta^{ij})$ and $C_{-1}^{ij}(\alpha^{ij}, \beta^{ij})$ respectively by $C_2^{ij}(\alpha^{ij}, \beta^{ij})$ and $C_{-2}^{ij}(\alpha^{ij}, \beta^{ij})$. We obtain

$$\begin{aligned} \Lambda_1(t) = & \frac{1}{4\sqrt{6}} \sum_{i \neq j} [C_{-1}^{ij}(\alpha^{ij}, \beta^{ij}) e^{i\gamma^{ij}} (\frac{1}{i\omega_R})(e^{i\omega_R t} - 1)] (I_{XX}^{ij} + I_{YY}^{ij} - 2I_{ZZ}^{ij}) + \\ & + \frac{1}{4\sqrt{6}} \sum_{i \neq j} [-C_1^{ij}(\alpha^{ij}, \beta^{ij}) e^{-i\gamma^{ij}} (\frac{1}{i\omega_R})(e^{-i\omega_R t} - 1)] (I_{XX}^{ij} + I_{YY}^{ij} - 2I_{ZZ}^{ij}) \\ & + \frac{1}{4\sqrt{6}} \sum_{i \neq j} [-C_2^{ij}(\alpha^{ij}, \beta^{ij}) e^{-2i\gamma^{ij}} (\frac{1}{2i\omega_R})(e^{-2i\omega_R t} - 1) + \\ & C_{-2}^{ij}(\alpha^{ij}, \beta^{ij}) e^{2i\gamma^{ij}} (\frac{1}{2i\omega_R})(e^{2i\omega_R t} - 1)] (I_{XX}^{ij} + I_{YY}^{ij} - 2I_{ZZ}^{ij}) \\ & - \sum_{m=-\infty}^{+\infty} \frac{1}{im\omega_R} (e^{-im\omega_R t} - 1) [\frac{3}{2\sqrt{6}} \sum_{i \neq j} b_{ij} e^{-im\gamma^{ij}} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij}] (I_{YY}^{ij} - I_{XX}^{ij}) \end{aligned} \quad (102)$$

The second order term F_2 due to the contribution of the Floquet-Magnus expansion can also be easily derived from Eq. (78) by making a similar substitution as above and we obtain

$$\begin{aligned} F_2 = & \frac{-\tau_R}{64\pi^2} \sum_{i \neq j} b_{ij} (C_2^{ij} - C_{-2}^{ij}) [C_{-1}^{ij}(\alpha^{ij}, \beta^{ij}) e^{i\gamma^{ij}} - C_1^{ij}(\alpha^{ij}, \beta^{ij}) e^{-i\gamma^{ij}}] [H_{ZQ}^{ij}, H_{DQ}^{ij}] \\ & - \frac{\tau_R}{32\pi^2} \sum_{i \neq j} b_{ij} (C_2^{ij} - C_{-2}^{ij}) [-C_2^{ij}(\alpha^{ij}, \beta^{ij}) e^{-2i\gamma^{ij}} + C_{-2}^{ij}(\alpha^{ij}, \beta^{ij}) e^{2i\gamma^{ij}}] [H_{ZQ}^{ij}, H_{DQ}^{ij}] \end{aligned} \quad (103)$$

The second order term $\Lambda_2(t)$ due to the contributions of the Floquet-Magnus expansion can also be calculated using Eq. (12), but it is less useful. We obtain the following

$$\begin{aligned}
\Lambda_2(t) = & \left[\frac{-1}{32\omega_R^2} \sum_{i \neq j} \left(b_{ij} \sum_{n=-2}^2 C_n^{ij} \right) \left(- \sum_{m=-\infty}^{+\infty} \frac{1}{m} \left[\sum_{i \neq j} b_{ij} e^{-im\gamma^{ij}} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij} \right] \right) \right] * \\
& * \left[\frac{1}{(n+m)} \right] [H_{ZQ}^{ij}, H_{DQ}^{ij}] \\
& + \left[\frac{-1}{32\omega_R^2} \sum_{i \neq j} \left(b_{ij} \sum_{n=-2}^2 C_n^{ij} \right) \left(- \sum_{m=-\infty}^{+\infty} \frac{1}{m} \left[\sum_{i \neq j} b_{ij} e^{-im\gamma^{ij}} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij} \right] \right) \right] * \\
& * \left[\frac{-1}{(n+m)} e^{-(n+m)i\omega_R t} \right] [H_{ZQ}^{ij}, H_{DQ}^{ij}] \\
& + \left[\frac{-1}{32\omega_R^2} \sum_{i \neq j} \left(b_{ij} \sum_{n=-2}^2 C_n^{ij} \right) \left(- \sum_{m=-\infty}^{+\infty} \frac{1}{m} \left[\sum_{i \neq j} b_{ij} e^{-im\gamma^{ij}} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij} \right] \right) \right] * \\
& * \left[\frac{1}{n} (e^{-in\omega_R t} - 1) \right] [H_{ZQ}^{ij}, H_{DQ}^{ij}] \\
& + \frac{1}{16\pi i \omega^2} \sum_{i \neq j} b_{ij} (C_2^{ij} - C_{-2}^{ij}) \left[\sum_{i \neq j} \frac{1}{4} C_{-1}^{ij} e^{i\gamma^{ij}} (e^{i\omega_R t} - 1) + \right. \\
& \left. \sum_{i \neq j} \frac{1}{4} C_1^{ij} e^{-i\gamma^{ij}} (e^{-i\omega_R t} - 1) \right] [H_{ZQ}^{ij}, H_{DQ}^{ij}] \\
& + \frac{1}{16\pi i \omega^2} \sum_{i \neq j} b_{ij} (C_2^{ij} - C_{-2}^{ij}) \left[\sum_{i \neq j} C_2^{ij} e^{-2i\gamma^{ij}} (e^{-2i\omega_R t} - 1) + \right. \\
& \left. \sum_{i \neq j} C_{-2}^{ij} e^{2i\gamma^{ij}} (e^{2i\omega_R t} - 1) \right] [H_{ZQ}^{ij}, H_{DQ}^{ij}] \\
& + \frac{1}{64\omega_R^2} \sum_{m=-\infty}^{+\infty} e^{-im\gamma^{ij}} \sum_{i \neq j} b_{ij} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij} * \\
& * \left[C_{-1}^{ij} e^{i\gamma^{ij}} - C_1^{ij} e^{-i\gamma^{ij}} - C_2^{ij} e^{-2i\gamma^{ij}} + C_{-2}^{ij} e^{2i\gamma^{ij}} \right] \left[\frac{e^{(2-m)i\omega_R t}}{(2-m)} \right] [H_{ZQ}^{ij}, H_{DQ}^{ij}] \\
& + \frac{1}{64\omega_R^2} \sum_{m=-\infty}^{+\infty} e^{-im\gamma^{ij}} \sum_{i \neq j} b_{ij} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij} * \\
& * \left[C_{-1}^{ij} e^{i\gamma^{ij}} - C_1^{ij} e^{-i\gamma^{ij}} - C_2^{ij} e^{-2i\gamma^{ij}} + C_{-2}^{ij} e^{2i\gamma^{ij}} \right] \left[\frac{-1}{(2-m)} \right] [H_{ZQ}^{ij}, H_{DQ}^{ij}] \\
& + \frac{1}{64\omega_R^2} \sum_{m=-\infty}^{+\infty} e^{-im\gamma^{ij}} \sum_{i \neq j} b_{ij} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij} * \\
& * \left[C_{-1}^{ij} e^{i\gamma^{ij}} - C_1^{ij} e^{-i\gamma^{ij}} - C_2^{ij} e^{-2i\gamma^{ij}} + C_{-2}^{ij} e^{2i\gamma^{ij}} \right] \left[\frac{(e^{-im\omega_R t} - 1)}{m} \right] [H_{ZQ}^{ij}, H_{DQ}^{ij}] \\
& m \neq 0, m \neq 2, m \neq -n
\end{aligned} \tag{104}$$

II – B – 3 COMPARISON OF BOTH BABA and BABA 2 PULSE SEQUENCES

The amplitude of the BABA and BABA2 DQ Hamiltonian depend on the angle γ , a fact which is supposed [5, 8] to lead to a comparatively low efficiency for multiple quantum excitation in powder samples, since most molecular orientations experience poor dipolar recoupling. Nevertheless, not only is the functional dependence on γ important, but also the strength of the DQ Hamiltonian that is tailored from the secular dipolar Hamiltonian by these BABA sequences. It is remarkable that, based on the strength of the dipolar DQ Hamiltonian, comparing Eqs. (56) and (101), the BABA2 pulse sequence should give more efficient recoupling than the BABA pulse sequence.

II – B – 4 APPLICATION OF THE FLOQUET - MAGNUS EXPANSION TO C7

The structure of the C7 cycles is shown in Fig. 3. In this recoupling sequence, seven RF cycles are timed to occupy two rotational periods, $2\tau_R$ [9]. The overall phase of each consecutive cycle, ϕ , is incremented in steps of $2\frac{\pi}{7}$. The RF amplitude throughout the

sequence satisfies the condition $\omega_{rf}^s - 7\omega_R$. The two rotational periods, each of duration $\left| \frac{2\pi}{\omega_R} \right|$, are subdivided into seven equal segments of duration $\tau_C = \frac{2\tau_R}{7}$. In this article, each element C_ϕ is comprised of two RF pulses, both with flip angle $\left| \frac{\omega_{IS} \tau_c}{2} \right| = 2\pi$, but with RF phases

differing by π , i.e. $C_{\varphi} = 2\pi\varphi 2\pi\varphi + \pi$ in conventional pulse sequence notation. The theory behind the $C7$ cycles is summarized as: a sequence of n radiofrequency cycles C_{φ_p} is considered in the general situation, with $p = 0, \dots, n-1$. p is timed to occupy N rotational periods. Each cycle C has duration $\tau_C = \frac{N\tau_R}{n}$ and an overall RF phase $\phi_p = \frac{2\pi p}{n}$. With the initial RF sequence starting at a time t^0 , then the p^{th} RF cycle C_{φ_p} runs between time points t_p^0 and t_{p+1}^0 , where $t_p^0 = t^0 + p\tau_C$. In this scheme of $C7$ sequences, the general form of the Hamiltonian of the spin-pair system expressed in the interaction frame of the RF field is given by

$$\tilde{H}_D(t) = \sum_Q \sum_{\lambda\mu lm} \tilde{\omega}_{\lambda\mu lm}^Q(t - t_p^0) e^{i(Nm - \mu)\phi_p} T_{\lambda\mu}^Q, \quad (105)$$

with

$$\phi_p = 2\pi \frac{p}{n}. \quad (106)$$

Q represents the indexes of different types of interaction ($Q = i, j$ or ij), l is the rank of the interaction with respect to rotations of the sample, m is the spatial rotational component ($m = -l, \dots, l$), λ is the rank of the interaction with respect to rotations of the spin polarizations and μ is the spin rotational component ($\mu = -\lambda, \dots, \lambda$). The amplitudes of the interaction frame Hamiltonian terms are given in general by

$$\tilde{\omega}_{\lambda\mu lm}^Q(\tau) = i^\mu d_{\mu 0}^\lambda(-\beta_{rf}(\tau)) \omega_{\lambda 0 lm}^Q e^{im\omega_R(\tau + t^0)} \quad (107)$$

Where $d_{\mu 0}^\lambda$ is a reduced Wigner function and β_{rf} is the overall spin rotation angle induced by the RF field given for the specific sequence $C_{\varphi} = 2\pi\varphi 2\pi\varphi + \pi$, by

$$\beta_{rf}(\tau) = 4\pi \frac{\tau}{\tau_C}, \text{ if } 0 \leq \tau < \frac{\tau_C}{2} \quad (108)$$

and

$$\beta_{rf}(\tau) = 4\pi \left(1 - \frac{\tau}{\tau_C}\right) \text{ if } \frac{\tau_C}{2} \leq \tau < \tau_C \quad (109)$$

In this article, we are concerned with the spin-pair interacting ($Q = ij$), the DQ dipolar recoupling ($\lambda = 2, \mu = 2$), and the direct dipole-dipole coupling space of rank 2 ($l = 2$). We are working with the first type of γ -encoded DQ recoupling sequence called $m = 1$. In summary, the sequence is $C7_2^1$ with, the following

$$Q = ij, \lambda = 2, \mu = \pm 2, l = 2, m = \pm 1 \quad (110)$$

Substituting these new values into Eq. (107), we obtained

$$\tilde{\omega}_{2\pm 22m}^{ij}(\tau) = i^2 d_{20}^2(-\beta_{rf}(\tau)) \omega_{202m}^{ij} e^{im\omega_R(\tau+t^0)} \quad (111)$$

where,

$$\omega_{202m}^{ij} = (\omega_{202-m}^{ij})^* = \sqrt{6} b_{ij} d_{0m}^2(\beta_{PR}) e^{-im\gamma_{PR}} d_{m0}^2(\beta_{RL}), \quad (112)$$

and

$$b_{ij} = -\frac{\mu_0 \gamma_i \gamma_j \hbar}{4\pi r_{ij}^3}. \quad (113)$$

b_{ij} is the dipole-dipole coupling constant. β_{RL} is the angle between the spinning axis and the main field ($\beta_{RL} = \arctan \sqrt{2}$, magic-angle spinning), with

$$m=0, \omega_{2020}^{ij} = \omega_{1020}^{ij} = 0. \quad (114)$$

β_{PR} and γ_{PR} are Euler angles specifying the relative orientation of the principal axis frame of the dipolar interaction P and a rotor-fixed frame R. Both angles (β_{PR} and γ_{PR}) are random variables in a powder sample. The Hamiltonian of the spin-pair system, expressed in the toggling frame of the RF field is written as

$$\tilde{H}_p(\tau) = \sum_{ij} \sum_{\mu m} \tilde{\omega}_{2\mu 2m}^{ij}(\tau) e^{i2\pi(Nm-\mu)\frac{p}{n}} T_{2\mu}^{ij} \quad (115)$$

The spin dynamics under the pulse sequence may also be investigated by using an alternative method such as the FT or FME which have advantages in some circumstances.

The calculation of F_1 (Eq. 11) over the p^{th} cycle ($t_p^0 \leq t < t_{p+1}^0$) for the

first order contribution to the FME leads to

$$F_{1p} = \frac{1}{\tau_C} \int_0^{\tau_C} \tilde{H}_p(\tau) d\tau = \sum_{ijm} e^{i2\pi(Nm-\mu)\frac{p}{n}} T_{2\mu}^{ij} \left(\frac{1}{\tau_C} \right) \int_0^{\tau_C} \tilde{\omega}_{2\mu 2m}^{ij}(\tau) d\tau \quad (116)$$

where

$$\bar{\omega}_{2\mu 2m}^{ij} = \frac{1}{\tau_C} \int_0^{\tau_C} \tilde{\omega}_{2\mu 2m}^{ij}(\tau) d\tau \quad (117)$$

Accounting for F_1 over the whole sequence, we have

$$F_1 = \frac{1}{n} \sum_{p=0}^{n-1} F_{1p} = \frac{1}{n} \sum_{p=0}^{n-1} \sum_{ij\mu m} \bar{\omega}_{2\mu 2m}^{ij} T_{2\mu}^{ij} e^{-i2\pi(Nm-\mu)\frac{p}{n}} = \frac{1}{n} \sum_{ij\mu m} \bar{\omega}_{2\mu 2m}^{ij} T_{2\mu}^{ij} \sum_{p=0}^{n-1} e^{i2\pi(Nm-\mu)\frac{p}{n}} \quad (118)$$

which produces

$$F_1 = \frac{1}{n} \sum_{ij21} \bar{\omega}_{2221}^{ij} T_{22}^{ij} \sum_{p=0}^{n-1} e^{i2\pi(N-2)\frac{p}{n}} + \frac{1}{n} \sum_{ij-2-1} \bar{\omega}_{2-22-1}^{ij} T_{2-2}^{ij} \sum_{p=0}^{n-1} e^{i2\pi(-N+2)\frac{p}{n}} \\ = \frac{1}{7} \sum_{ij21} \bar{\omega}_{2221}^{ij} T_{22}^{ij} + \frac{1}{7} \sum_{ij-2-1} \bar{\omega}_{2-22-1}^{ij} T_{2-2}^{ij} \quad (119)$$

We can evaluate $\bar{\omega}_{2221}^{ij}$ by using Eq. (117)

$$\bar{\omega}_{2221}^{ij} = \frac{1}{2\tau_R} \left[\int_0^{\frac{2\tau_R}{7}} \tilde{\omega}_{2221}^{ij}(\tau) d\tau + \int_{\frac{2\tau_R}{7}}^{\frac{4\tau_R}{7}} \tilde{\omega}_{2221}^{ij}(\tau) d\tau + \int_{\frac{4\tau_R}{7}}^{\frac{6\tau_R}{7}} \tilde{\omega}_{2221}^{ij}(\tau) d\tau + \int_{\frac{6\tau_R}{7}}^{\frac{8\tau_R}{7}} \tilde{\omega}_{2221}^{ij}(\tau) d\tau \right] \\ + \frac{1}{2\tau_R} \left[\int_{\frac{8\tau_R}{7}}^{\frac{10\tau_R}{7}} \tilde{\omega}_{2221}^{ij}(\tau) d\tau + \int_{\frac{10\tau_R}{7}}^{\frac{12\tau_R}{7}} \tilde{\omega}_{2221}^{ij}(\tau) d\tau + \int_{\frac{12\tau_R}{7}}^{\frac{14\tau_R}{7}} \tilde{\omega}_{2221}^{ij}(\tau) d\tau \right] \quad (120)$$

With $\tilde{\omega}_{2221}^{ij}(\tau)$ obtained from Eq. (111)

$$\tilde{\omega}_{2221}^{ij}(\tau) = i^2 d_{20}^2 (-\beta_{rf}(\tau)) \omega_{2021}^{ij} e^{i\omega_R(\tau+t^0)} = \frac{9}{16} \sin(2\beta_{RL}) b_{ij} \sin^2(\beta_{rf}) e^{i\omega_R\tau} e^{i(\omega_R t^0 - \gamma_{PR})} \sin(2\beta_{PR}) \quad (121)$$

where the relevant Wigner matrix elements (see appendix A2) have been used. $\tilde{\omega}_{2221}^{ij}(\tau)$ Can be written in the following form for integration purposes

$$\tilde{\omega}_{2221}^{ij}(\tau) = A \sin^2(\beta_{rf}) e^{i\omega_R\tau} = -\frac{A}{4} (e^{2i\beta_{rf}} + e^{-2i\beta_{rf}} - 2) e^{i\omega_R\tau} \quad (122)$$

with,

$$A = \frac{9}{16} \sin(2\beta_{RL}) b_{ij} e^{i(\omega_R t^0 - \gamma_{PR})} \sin(2\beta_{PR}) \quad (123)$$

The result of each individual integral term of the Eq. (120) is

$$\int_0^{\frac{2\tau_R}{7}} \tilde{\omega}_{2221}^{ij}(\tau) d\tau = \frac{A7\tau_C784}{8\pi} \left(\frac{e^{\frac{i\pi}{14}} + i}{780} \right) \quad (124)$$

Using the fact that,

$$\sin(2\arctan(x)) = \frac{2x}{1+x^2}, \quad (125-a)$$

i.e.

$$\sin(2\beta_{RL}) = \sin(2\arctan \sqrt{2}) = \frac{2}{3} \sqrt{2}, \quad (125-b)$$

we have

$$A = \frac{3}{8} \sqrt{2} b_{ij} e^{i(\omega_R t^0 - \gamma_{PR})} \sin(2\beta_{PR}) \quad (126)$$

and finally, we obtain

$$\bar{\omega}_{2221}^{ij} = \frac{343}{520\pi\sqrt{2}} (e^{i\frac{\pi}{14}} + i) b_{ij} e^{i(\omega_R t^0 - \gamma_{PR})} \sin(2\beta_{PR}) = (\bar{\omega}_{2-22-1}^{ij})^* \quad (127)$$

Y. K. Lee et al. [9] derived a similar expression. Using the first contributions to the FME Eqs. (10)–(13) we obtain the following results

$$F_1 = \frac{1}{7} \sum_{ij} \frac{343(i + e^{i\frac{\pi}{14}})}{520\pi\sqrt{2}} b_{ij} e^{i(\omega_R t^0 - \gamma_{PR})} \sin(2\beta_{PR}) T_{22}^{ij} + \frac{1}{7} \sum_{ij} \frac{343(-i + e^{-i\frac{\pi}{14}})}{520\pi\sqrt{2}} b_{ij} e^{-i(\omega_R t^0 - \gamma_{PR})} \sin(2\beta_{PR}) T_{2-2}^{ij} \quad (128)$$

$$\begin{aligned} \Lambda_1(t) = & \frac{1}{7} \sum_{ij} \frac{21\sqrt{2}i\tau_C}{64\pi} b_{ij} e^{i(\omega_R t^0 - \gamma_{PR})} \sin(2\beta_{PR}) \left(\frac{1}{30} e^{\frac{i60\pi t}{7\tau_C}} - \frac{1}{26} e^{\frac{i52\pi t}{7\tau_C}} - e^{\frac{i4\pi t}{7\tau_C}} \right) T_{22}^{ij} \\ & + \frac{1}{7} \sum_{ij} \frac{343i\tau_C}{520\pi\sqrt{2}} b_{ij} e^{i(\omega_R t^0 - \gamma_{PR})} \sin(2\beta_{PR}) T_{22}^{ij} \\ & + \frac{1}{7} \sum_{ij} \frac{-21\sqrt{2}i\tau_C}{64\pi} b_{ij} e^{-i(\omega_R t^0 - \gamma_{PR})} \sin(2\beta_{PR}) \left(\frac{1}{30} e^{-\frac{i60\pi t}{7\tau_C}} - \frac{1}{26} e^{-\frac{i52\pi t}{7\tau_C}} - e^{-\frac{i4\pi t}{7\tau_C}} \right) T_{2-2}^{ij} \\ & + \frac{1}{7} \sum_{ij} \frac{-343i\tau_C}{520\pi\sqrt{2}} b_{ij} e^{-i(\omega_R t^0 - \gamma_{PR})} \sin(2\beta_{PR}) T_{2-2}^{ij} - tF_1, \end{aligned} \quad (129)$$

$$\begin{aligned} F_2 = & \sum_{ij} \left[\frac{-449A_2 A e^{i10\frac{\pi}{7}}}{7200\pi\omega_R} - \frac{2\pi A_2 A e^{i4\frac{\pi}{7}}}{\sqrt{2}3549\pi\omega_R} + \frac{152212\pi A_2 A}{798525\sqrt{2}\pi\omega_R} - \frac{49iA_2 A}{1365\omega_R} - \frac{\pi A_2 B_2}{7\omega_R} \right] [T_{22}^{ij}, T_{2-2}^{ij}] \\ & + \sum_{ij} \left[\frac{49A^2}{454272\omega_R} (1 - e^{i8\frac{\pi}{7}}) + \frac{343A^2}{\pi 76050\omega_R} (1 - e^{i4\frac{\pi}{7}}) - \frac{7B_2}{4\pi\omega_R} (4i\frac{\pi}{7}) e^{i4\frac{\pi}{7}} \right] [T_{22}^{ij}, T_{2-2}^{ij}] \\ & + \sum_{ij} \left[\frac{i\pi 61A^2}{11760\omega_R} + \frac{7B_2}{1800\pi\omega_R} (60i\frac{\pi}{7}) e^{i4\frac{\pi}{7}} - \frac{7B_2}{1352\pi\omega_R} (52i\frac{\pi}{7}) e^{i4\frac{\pi}{7}} - C.C \right] [T_{22}^{ij}, T_{2-2}^{ij}] \\ & + \frac{1}{2} [A_2 + \frac{49A}{390\pi} (i + e^{i\frac{\pi}{14}})] [T_{22}^{ij}, \Lambda_1(0)] - \frac{1}{2} [A_2 + \frac{49A}{390\pi} (-i + e^{-i\frac{\pi}{14}})] [T_{2-2}^{ij}, \Lambda_1(0)] \end{aligned} \quad (130)$$

and

$$\begin{aligned}
\Lambda_2(t) = & \sum_{ij} \left[\frac{a_{ij} A_2}{2400 \sqrt{2} \omega_R^2} (e^{-i15\omega_R t} - 1) - \frac{3a_{ij} A_2}{5408 \sqrt{2} \omega_R^2} (e^{-i13\omega_R t} - 1) - \frac{3a_{ij} A_2}{16 \sqrt{2} \omega_R^2} (e^{-i\omega_R t} - 1) \right] * \\
& * [T_{22}^{ij}, T_{2-2}^{ij}] \\
& - \sum_{ij} \left[\frac{7ia_{ij} A_2 t}{130 \sqrt{2} \omega_R} + \frac{A_2 B_2 t^2}{2} + \frac{3 \sqrt{2} a_{ij} A}{163072 \omega_R^2} (e^{i2\omega_R t} - 1) - \frac{3 \sqrt{2} a_{ij} A}{43904 \omega_R^2} (e^{i14\omega_R t} - 1) \right] * \\
& * [T_{22}^{ij}, T_{2-2}^{ij}] \\
& + \sum_{ij} \left[\frac{-\sqrt{2} a_{ij} A}{878080 \omega_R^2} (e^{-i28\omega_R t} - 1) + \frac{3 \sqrt{2} a_{ij} A}{2119936 \omega_R^2} (e^{-i26\omega_R t} - 1) + \frac{3 \sqrt{2} a_{ij} A}{43904 \omega_R^2} (e^{-i14\omega_R t} - 1) \right] * \\
& * [T_{22}^{ij}, T_{2-2}^{ij}] \\
& + \sum_{ij} \left[\frac{-\sqrt{2} a_{ij} A}{219520 \omega_R^2} (e^{-i14\omega_R t} - 1) - \frac{\sqrt{2} a_{ij} A}{163072 \omega_R^2} (e^{-i12\omega_R t} - 1) + \frac{49 a_{ij} A}{7800 \sqrt{2} \omega_R^2} (e^{-i15\omega_R t} - 1) \right] * \\
& * [T_{22}^{ij}, T_{2-2}^{ij}] \\
& - \sum_{ij} \left[\frac{49 a_{ij} A}{6760 \sqrt{2} \omega_R^2} (e^{-i13\omega_R t} - 1) + \frac{49 a_{ij} A}{260 \sqrt{2} \omega_R^2} (e^{i\omega_R t} - 1) + \frac{B_2 A}{14 \omega_R^2} (i\omega_R t) e^{i\omega_R t} \right] * \\
& * [T_{22}^{ij}, T_{2-2}^{ij}] \\
& + \sum_{ij} \left[\frac{B_2 A}{6300 \omega_R^2} (i15\omega_R t) e^{i15\omega_R t} - \frac{B_2 A}{4732 \omega_R^2} (i13\omega_R t) e^{-i13\omega_R t} \right] [T_{22}^{ij}, T_{2-2}^{ij}] \\
& - C.C. [T_{22}^{ij}, T_{2-2}^{ij}] - t F_2 + \left[\frac{7A_2 t}{2} - \frac{A}{i120\omega_R} (e^{i15\omega_R t} - 1) + \frac{A}{i104\omega_R} (e^{-i13\omega_R t} - 1) \right] [T_{22}^{ij}, \Lambda_1(0)] \\
& + \left[\frac{A}{4i\omega_R} (e^{i\omega_R t} - 1) \right] [T_{22}^{ij}, \Lambda_1(0)] + C.C. [T_{2-2}^{ij}, \Lambda_1(0)]
\end{aligned} \quad (131)$$

where the constants are

$$a_{ij} = b_{ij} e^{i(\omega_R t^0 - \gamma_{PR}^{ij})} \sin(2\beta_{PR}) \quad (132)$$

$$A = \frac{3}{8} \sqrt{2} a_{ij} \quad (133)$$

$$A_2 = \frac{1}{7} \sum_{ij} \frac{343(i + e^{i\frac{\pi}{14}})}{520\pi \sqrt{2}} a_{ij}, B_2 = A_2 * \quad (134)$$

With

$$T_{22}^{ij} = \frac{1}{2} I_+^i I_+^j, \quad (135)$$

$$T_{2-2}^{ij} = \frac{1}{2} I_-^i I_-^j \quad (136)$$

and C.C. is the complex conjugated.

NUMERICAL ANALYSIS OF C7—The functions $\Lambda_1(t)$ and $\Lambda_2(t)$ written in terms of the rotor period (real, imaginary and absolute part) are plotted versus the dimensionless number $\phi = \frac{t}{\tau_R}$. Assuming a system of two spins, we have:

$$\frac{F_1}{a_{ij}} = \frac{1}{7} \frac{343(i + e^{i\frac{\pi}{14}})}{520\pi\sqrt{2}} T_{22}^{ij} + \frac{1}{7} \frac{343(-i + e^{-i\frac{\pi}{14}})}{520\pi\sqrt{2}} T_{2-2}^{ij} \quad (137)$$

$$\frac{\Lambda_1(t)}{\alpha_{ij}\tau_R} = C7_1(\phi) = \left[\frac{3i}{112\sqrt{2}\pi} \left(\frac{1}{30} e^{i30\pi\phi} - \frac{1}{26} e^{i26\pi\phi} - e^{i2\pi\phi} \right) + \frac{49}{520\sqrt{2}\pi} \left(\frac{2i}{7} - \phi \left(i + e^{i\frac{\pi}{4}} \right) \right) \right] T_{22}^{ij} \\ + \left[\frac{-3i}{112\sqrt{2}\pi} \left(\frac{1}{30} e^{-i30\pi\phi} - \frac{1}{26} e^{-i26\pi\phi} - e^{-i2\pi\phi} \right) + \frac{49}{520\sqrt{2}\pi} \left(\frac{-2i}{7} - \phi \left(-i + e^{-i\frac{\pi}{4}} \right) \right) \right] T_{2-2}^{ij} \quad (138)$$

$$\overline{F_2} = \frac{F_2}{a_{ij}^2\tau_R} = \left[\frac{-449A_2Ae^{i10\frac{\pi}{7}}}{14400\pi^2} - \frac{A_2Ae^{i4\frac{\pi}{7}}}{\sqrt{23549}} + \frac{76106A_2A}{798525\sqrt{2}} - \frac{49iA_2A}{2730\pi} - \frac{A_2B_2}{14} \right] \underbrace{[T_{22}^{ij}, T_{2-2}^{ij}]}_{DQ} \\ + \left[\frac{49A^2}{908544\pi} (1 - e^{i8\frac{\pi}{7}}) + \frac{343A^2}{\pi^2 152100} (1 - e^{i4\frac{\pi}{7}}) - \frac{7B_2}{8\pi} \left(i\frac{4}{7} \right) e^{i4\frac{\pi}{7}} \right] \underbrace{[T_{22}^{ij}, T_{2-2}^{ij}]}_{DQ} \quad (139) \\ + \left[\frac{i61A^2}{23520} + \frac{7B_2}{1800\pi} \left(i\frac{30}{7} \right) e^{i4\frac{\pi}{7}} - \frac{7B_2}{1352\pi} \left(i\frac{26}{7} \right) e^{i4\frac{\pi}{7}} \right] \underbrace{[T_{22}^{ij}, T_{2-2}^{ij}]}_{DQ} - C.C. \underbrace{[T_{22}^{ij}, T_{2-2}^{ij}]}_{DQ}$$

and

$$\frac{\Lambda_2(t)}{a_{ij}^2\tau_R^2} = C7_2(\phi) = \frac{1}{4\pi^2} \left[\frac{A_2}{2400\sqrt{2}} (e^{i30\pi\phi} - 1) - \frac{3A_2}{5408\sqrt{2}} (e^{-i26\pi\phi} - 1) - \frac{3A_2}{16\sqrt{2}} (e^{-i2\pi\phi} - 1) \right] * \\ * \underbrace{[T_{22}^{ij}, T_{2-2}^{ij}]}_{DQ} \\ - \frac{1}{4\pi^2} \left[\frac{7iA_22\pi\phi}{130\sqrt{2}} + 2A_2B_2\pi^2\phi^2 + \frac{3\sqrt{2}A}{163072} (e^{i4\pi\phi} - 1) - \frac{3\sqrt{2}A}{43904} (e^{i28\pi\phi} - e^{-i28\pi\phi}) \right] * \\ * \underbrace{[T_{22}^{ij}, T_{2-2}^{ij}]}_{DQ} \\ + \frac{1}{4\pi^2} \left[\frac{-\sqrt{2}A}{878080} (e^{-i56\pi\phi} - 1) + \frac{3\sqrt{2}A}{2119936} (e^{-i52\pi\phi} - 1) + \frac{\sqrt{2}A}{219520} (e^{-i28\pi\phi} - 1) \right] * \\ * \underbrace{[T_{22}^{ij}, T_{2-2}^{ij}]}_{DQ} \quad (140) \\ + \frac{1}{4\pi^2} \left[-\frac{\sqrt{2}A}{163072} (e^{i24\pi\phi} - 1) + \frac{49A}{7800\sqrt{2}} (e^{-i30\pi\phi} - 1) + \frac{49A}{6760\sqrt{2}} (e^{-i26\pi\phi} - 1) \right] * \\ * \underbrace{[T_{22}^{ij}, T_{2-2}^{ij}]}_{DQ} \\ - \frac{1}{4\pi^2} \left[\frac{49A}{260\sqrt{2}} (e^{i2\pi\phi} - 1) + \frac{B_2A}{14} (i2\pi\phi) e^{i2\pi\phi} + \frac{B_2A}{6300\omega_R^2} (i30\pi\phi) e^{i30\pi\phi} \right] \underbrace{[T_{22}^{ij}, T_{2-2}^{ij}]}_{DQ} \\ + \frac{1}{4\pi^2} \left[-\frac{B_2A}{4732} (i26\pi\phi) e^{-i26\pi\phi} \right] \underbrace{[T_{22}^{ij}, T_{2-2}^{ij}]}_{DQ} - C.C. \underbrace{[T_{22}^{ij}, T_{2-2}^{ij}]}_{DQ} - \phi \overline{F_2}$$

where the constants are

$$a_{ij} = b_{ij} e^{i(\omega_R t^0 - \gamma_{PR}^{ij})} \sin(2\beta_{PR}) \quad (141)$$

$$A = \frac{3}{8} \sqrt{2} \quad (142)$$

$$A_2 = \frac{1}{7} \frac{343(i + e^{i\frac{\pi}{14}})}{520\pi\sqrt{2}}, \quad (143-a)$$

$$B_2 = A_2^* \quad (143-b)$$

and C.C. means complex conjugate.

Analysis of the figures: A similar analysis previously done for the BABA sequence can also be extended to the C7 sequence. Figs. 5a, 5b, and 5c show respectively, the graphs of the functions $\frac{\Lambda_1(t)}{a_{ij}\tau_R} = C7_1(\phi)$, $\frac{\Lambda_2(t)}{a_{ij}^2\tau_R^2} = C7_2(\phi)$ and $(C7_1(\phi), C7_2(\phi))$ as a function of $\phi = \frac{t}{\tau_R}$. A closer look at Fig. 5c shows that the magnitude of $C7_2(\phi)$ is small in comparison to the

magnitude of $C7_1(\phi)$, i.e. $\left| \frac{\Lambda_2(t)}{a_{ij}^2\tau_R^2} \right| < \left| \frac{\Lambda_1(t)}{a_{ij}\tau_R} \right|$ as expected. As a result, $\Lambda_2(t)$ will be less useful in many cases. We can also observe that all graphs are strictly monotonous. This tells us that, the “weight” of DQ terms increases continuously with time and no decoupling condition occurs in this scheme.

III. COMPARISON BETWEEN BABA AND C7 PULSE SEQUENCES

For a direct comparison between BABA and C7, if we consider only the central term corresponding to $n' = 0$, and neglect all other terms, we have

$$C_1^{ij}(\alpha^{ij}, \beta^{ij}) = \frac{-1}{2\sqrt{2}} Y_{20} e^{-i\alpha^{ij}} \sin 2\beta^{ij} \quad (144)$$

and from an earlier report [24], $Y_{20} = \frac{1}{\sqrt{6}}(3\cos^2\Theta - 1)$, with Θ being one of the two angles that specify the direction of the internuclear vector in polar coordinates in the laboratory axis

system. For example, for a direction corresponding to $\Theta = 0$, $\left| \overline{H}_{DQ}^0 \right|_{BABA} \simeq 0.056 \sin \gamma^{ij}$ units and $\left| \overline{H}_{DQ}^0 \right|_{C7} \simeq 0.040$ units (see appendix A4). Eq. (175) shows that the amplitude of the BABA DQ Hamiltonian depends on the angle γ^{ij} , a fact that is supposed to lead to a comparatively low efficiency for MQ excitation in powder samples [5, 8, 9]. Instead, for C7 pulse sequence, Eqs. (128) and (174) show that, the γ -angle encoding takes place in the phase of the DQ Hamiltonian, resulting in a low sensitivity to the orientation of the internuclear vectors with respect to the rotor leading to a high overall efficiency for [9, 26–30]. It is well known in the NMR community that gamma-angle dependent sequences reach about 50% conversion efficiency, while gamma-angle independent sequences reach around 70% [5, 31, 32]. Even though the theoretical efficiency of the gamma-independent sequences is higher, the choice of one recoupling sequence in favor of another is not obvious. Therefore, it is essential to consider several other factors that lead to the excitation efficiency such as the magnitude of the homonuclear dipole-dipole coupling constant or the CSA interaction [5, 31] which is ignored in this article. In addition, this work presents only the analysis of the original C7 pulse sequence ($C7_2^1$). The basic construction principle of the

original C7 allows considerable freedom over the choice of the element C_φ . For instance, the new element referred to POST-C7 [5, 29] shows significant improvement to the robustness of the scheme with respect to chemical shift offsets and rf inhomogeneity.

For example, considering the strength of the DQ Hamiltonian (for example, the central term, $n' = 0$), the norms of the DQ Hamiltonians are related by

$\left\| \overline{H}_{DQ}^0 \right\|_{BABA} \simeq 1.4 \sin \gamma^{ij} \left\| \overline{H}_{DQ}^0 \right\|_{C7}$. This shows that both sequences have about the same efficiency, but with the strength of the DQ Hamiltonian of the BABA sequence proportional to $\sin \gamma^{ij}$. However, unlike the BABA pulse sequence, the C7 pulse sequence is extremely insensitive to chemical shifts and rf field errors [5, 8, 29]. Furthermore, if all terms in Eq. (175) are taken into account, the dynamics are more complex in BABA for given values of the angles that specify the direction of the internuclear vector. This may describe not only the buildup but also the destruction of DQ coherence during a rotor period. This yields the strength of the DQ Hamiltonian of the BABA sequence relatively smaller than that of the C7 sequence. As stated above, several other factors need to be considered as well for the comparison of both pulse sequences. Despite the fact that the CSA is ignored in this article, it is important to mention that the BABA pulse sequence is not really useful when the chemical shift anisotropies are big [5, 8].

The efficiency of the recoupling pulse sequences is indicated by double quantum terms.

Here, the magnitudes $\frac{\Lambda_1(t)}{b_{ij}\tau_R}$ for BABA and $\frac{\Lambda_1(t)}{a_{ij}\tau_R}$ for C7 determine the amplitude of the DQ coherence. This tells us about the potential degree to which the sequence is efficient. Therefore, the functions $\Lambda_1(t)$ and $\Lambda_2(t)$ are useful to study the spin dynamics and can be used as a viable approach to compare recoupling sequences. We have extended the description of DQ dynamics during dipolar recoupling beyond the first-order limit, which generally assumes chemical shift anisotropy effects are negligible comparatively to large dipolar couplings. For the first order terms, we have showed that C7 is a γ - independent recoupling sequence, since the norm of its DQ Hamiltonian is γ - independent

$$\left(\left\| \overline{H}_{DQ}^0 \right\|^{C7} = 0.040 b_{ij} \sin(2\beta_{PR}) \right).$$

IV. CONCLUSION

In this work, we use the Floquet-Magnus expansion approach to describe the spin dynamics in solid-state NMR. Whereas the AHT and FT Hamiltonians are in general connected with stroboscopic detection schemes, the FME instead provides, at least in principle, the option to evaluate the spin evolution between the time points of detection. To validate such a description, we used the examples of the dipolar interaction in a MAS with the BABA and the original C7 pulse sequences.

In contrast to the usual approaches (AHT and FT) used to control the dynamics of spin systems in solid-state NMR, the FME scheme overcomes the limitation of the stroboscopic detection schemes and simplifies calculations of “the points in between”, which is complicated using the FT [18]. In the FME approach, even when the first and second order F_1 and F_2 are identical to their counterparts in AHT and FT, the $\Lambda_n(t)$ ($n = 1, 2, 3, \dots$) functions provide a simple approach for evaluating the spin evolution during “the time in

between” through the Magnus expansion of the operator connected to this part of the evolution. $A_n(t)$ functions are connected to the appearance of features like spinning sidebands in MAS. The evaluation of $A_n(t)$ operator functions are useful especially for the analysis of the non-stroboscopic evolution. For example, in the case of C7, for non-stroboscopic detection scheme, they can be used to estimate the intensity of the spinning sidebands manifold. Higher order effects such as $(F_2, A_2(t))$, $(F_3, A_3(t))$ can also be evaluated using FME approach easier than in the case of AHT or FT.

We made an attempt to sketch out the FME technique and most of the conclusions derived from these pulse sequences can be obtained from AHT. This is in agreement with the AHT providing that the stroboscopic detection points is a particular case of FME. The FME approach in solid-state NMR spectroscopy provides new aspects not present in AHT and FT, namely the results of Eqs (10), (12), and (148). The fact that the F_n ($n = 1, 2, \dots$) expressions can also be obtained by AHT and FT makes the FME approach unique through its expressions for $A_n(t)$. We derived the expressions for $A_1(t)$ and $A_2(t)$ that are unique additions for AHT and FT. These functions are used to evaluate the spin behavior during or in between the RF pulses. Unlike in AHT where an evaluation of nested commutators and their painful double, triple and multiple integrals are required to obtain respectively the second, third and higher correction terms of a Hamiltonian, in Floquet-Magnus expansion only an evaluation of nested commutators with a single integral is required.

The paper describes the time evolution of the spin system at all times and offers a way to handle other similar approaches. We hope to approach other interesting problems that are amenable to the treatment presented here such as multi-mode Hamiltonian, rotational-resonance recoupling, continuous wave (CW) irradiation on a single species, DARR and MIRROR recoupling, simultaneous CW irradiation on two different spin species, phase-alternating (X_iX) irradiation on a single spin species, CW irradiation on one and (X_iX) irradiation on a second spin species, phase-modulated Lee-Goldburg decoupling, C-type and R-type sequences, TPPM decoupling... etc....

We recognize that the choice of the pulse sequences (BABA, C7) used in this paper may not be ideal due to lengthy calculations using FME comparatively to the choice of simple examples outlined in a recent report [7]. The possibility of enhanced FME performance certainly deserves further attention and additional quantitative work would demonstrate the utility of the Floquet-Magnus expansion in solid state NMR.

Acknowledgments

This work was supported by the French National Research Agency (ANR) under the «DESIRE» project. Eugene S. Mananga acknowledges also support from the Commissariat à l’Energie Atomique, NEUROSPIN, France.

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VI. APPENDIX

A0

$$T_3^{(2)} = \sum_{m=1}^1 [\Lambda_m, T_{3-m}^{(1)}] = [\Lambda_1, T_2^{(1)}] = [\Lambda_1, [\Lambda_1, F_1]] \quad (145)$$

$$\Lambda_3 = -F_3 - \frac{1}{2} (\underbrace{[\Lambda_2, A] + [\Lambda_2, F_1]}_{[\Lambda_2, A+F_1]} + [\Lambda_1, F_2]) + \frac{1}{12} (\underbrace{[\Lambda_1, [\Lambda_1, A]] - [\Lambda_1, [\Lambda_1, F_1]]}_{[\Lambda_1, [\Lambda_1, A]] + [\Lambda_1, [\Lambda_1, -F_1]]}) \quad (146)$$

After integration, we obtain the following result

$$\Lambda_3(t) = -tF_3 - \frac{1}{2} \int_0^t ([\Lambda_2, A + F_1] + [\Lambda_1, F_2]) dt' + \frac{1}{12} \int_0^t [\Lambda_1, [\Lambda_1, A - F_1]] dt' + \Lambda_3(0) \quad (147)$$

or

$$\Lambda_3(t) = \frac{1}{2} \int_0^t [A + F_1, \Lambda_2] dt' + \frac{1}{2} \int_0^t [F_2, \Lambda_1] dt' + \frac{1}{12} \int_0^t [\Lambda_1, [\Lambda_1, A - F_1]] dt' - tF_3 + \Lambda_3(0) \quad (148)$$

We can write the following, as previously described [6]

$$F_3 = \frac{\Omega_3(T)}{T}, \quad (149)$$

where

$$\begin{aligned} \Omega_3(T) &= \sum_{j=0}^2 \frac{B_j}{j!} \int_0^T S_3^{(j)}(\tau) d\tau \\ &= \frac{B_0}{0!} \int_0^T S_3^{(0)}(\tau) d\tau + \frac{B_1}{1!} \int_0^T S_3^{(1)}(\tau) d\tau + \frac{B_2}{2!} \int_0^T S_3^{(2)}(\tau) d\tau \\ &= \frac{-1}{2} \int_0^T S_3^{(1)}(\tau) d\tau + \frac{1}{12} \int_0^T S_3^{(2)}(\tau) d\tau \end{aligned} \quad (150)$$

$$S_3^{(1)} = W_3^{(1)}(t) + (-1)^{(2)} T_3^{(1)}(t) = W_3^{(1)}(t) + T_3^{(1)}(t) = [\Lambda_2, A] + [\Lambda_1, F_2] + [\Lambda_2, F_1] \quad (151)$$

$$S_3^{(1)} = [\Lambda_2, A + F_1] + [\Lambda_1, F_2] \quad (152)$$

$$S_3^{(2)} = W_3^{(2)}(t) + (-1)^{(3)} T_3^{(2)}(t) = W_3^{(2)}(t) - T_3^{(2)}(t) = \underbrace{[\Lambda_1, [\Lambda_1, A]] - [\Lambda_1, [\Lambda_1, F_1]]}_{[\Lambda_1, [\Lambda_1, A - F_1]]} \quad (153)$$

$$\Omega_3(T) = \frac{1}{2} \int_0^T [A + F_1, \Lambda_2] dt + \frac{1}{2} \int_0^T [F_2, \Lambda_1] dt + \frac{1}{12} \int_0^T [\Lambda_1, [\Lambda_1, A - F_1]] dt \quad (154)$$

Finally we obtain,

$$F_3 = \frac{1}{2T} \int_0^T [A + F_1, \Lambda_2] dt + \frac{1}{2T} \int_0^T [F_2, \Lambda_1] dt + \frac{1}{12T} \int_0^T [\Lambda_1, [\Lambda_1, A - F_1]] dt \quad (155-a)$$

We can also write the above Eqs. (147) and (155) in the following forms [7]

$$\Lambda_3(t) = \int_0^t G_3(\tau) d\tau - tF_3 + \Lambda_3(0) \quad (155-b)$$

$$G_3(\tau) = -\frac{i}{2} [H(\tau) + F_1, \Lambda_2(\tau)] - \frac{i}{2} [F_2, \Lambda_1(\tau)] - \frac{1}{12} [\Lambda_1(\tau), [\Lambda_1(\tau), H(\tau) - F_1]]. \quad (155-c)$$

$$\Lambda_3(T) = \Lambda_3(0) \quad (155-d)$$

and

$$F_3 = -\frac{i}{2T} \int_0^T [H(\tau) + F_1, \Lambda_2(\tau)] d\tau - \frac{i}{2T} \int_0^T [F_2, \Lambda_1(\tau)] d\tau - \frac{1}{12T} \int_0^T [\Lambda_1(\tau), [\Lambda_1, H(\tau) - F_1]] d\tau \quad (155-e)$$

A1

$$\begin{aligned} \int_0^T H_z B dt &= \int_0^{\tau_R} \left(\frac{1}{2} \sum_{i \neq j} \omega_D^{ij}(t) a_0 \frac{1}{\sqrt{6}} \right) \left(-\sum_{m=-\infty}^{+\infty} \frac{1}{im\omega_R} (e^{-im\omega_R t} - 1) \right) * \\ &\quad * \left[\frac{3}{2\sqrt{6}} \sum_{i \neq j} b_{ij} e^{-im\gamma^{ij}} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij} \right] dt \\ &= \frac{1}{4\sqrt{6}} \int_0^{\tau_R} \sum_{i \neq j} \omega_D^{ij}(t) \left(-\sum_{m=-\infty}^{+\infty} \frac{1}{im\omega_R} (e^{-im\omega_R t} - 1) \right) * \\ &\quad * \left[\frac{3}{2\sqrt{6}} \sum_{i \neq j} b_{ij} e^{-im\gamma^{ij}} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij} \right] dt \\ &= \frac{1}{4\sqrt{6}} \int_0^{\tau_R} \sum_{i \neq j} (b_{ij} \sum_{n=-2}^2 C_n^{ij} (\alpha^{ij}, \beta^{ij}, \gamma^{ij}) e^{-in\omega_R t}) \left(-\sum_{m=-\infty}^{+\infty} \frac{1}{im\omega_R} (e^{-im\omega_R t} - 1) \right) * \\ &\quad * \left[\frac{3}{2\sqrt{6}} \sum_{i \neq j} b_{ij} e^{-im\gamma^{ij}} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij} \right] dt \\ &= \frac{1}{16} \sum_{i \neq j} (b_{ij} \sum_{n=-2}^2 C_n^{ij} (\alpha^{ij}, \beta^{ij}, \gamma^{ij})) \left(-\sum_{m=-\infty}^{+\infty} \frac{1}{im\omega_R} * \right. \\ &\quad * \left. \left[\sum_{i \neq j} b_{ij} e^{-im\gamma^{ij}} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij} \right] \right) \underbrace{\int_0^{\tau_R} e^{-in\omega_R t} (e^{-im\omega_R t} - 1) dt}_{\equiv 0} \\ &= 0 \end{aligned} \quad (156)$$

$$\text{Since } \omega_R = \frac{2\pi N}{\tau_R}, N=0, 1, 2, \dots \quad (157)$$

Similarly,

$$\begin{aligned} \int_0^T H^m A dt &\int_0^{\tau_R} \left(\sum_{m=-\infty}^{+\infty} e^{-im(\omega_R t + \gamma^{ij})} \left[\frac{3}{2\sqrt{6}} \sum_{i \neq j} b_{ij} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij} \right] \right) * \\ &\quad * \left(\frac{1}{4\sqrt{6}} [C_{-2}^{ij} (\alpha^{ij}, \beta^{ij}) e^{2i\gamma^{ij}} \left(\frac{1}{2i\omega_R} \right) (e^{2i\omega_R t} - 1)] \right) dt \\ &+ \int_0^{\tau_R} \left(\sum_{m=-\infty}^{+\infty} e^{-im(\omega_R t + \gamma^{ij})} \left[\frac{3}{2\sqrt{6}} \sum_{i \neq j} b_{ij} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij} \right] \right) * \\ &\quad * \left(\frac{1}{4\sqrt{6}} [-C_2^{ij} (\alpha^{ij}, \beta^{ij}) e^{-2i\gamma^{ij}} \left(\frac{1}{2i\omega_R} \right) (e^{2i\omega_R t} - 1)] \right) dt \\ &+ \int_0^{\tau_R} \left(\sum_{m=-\infty}^{+\infty} e^{-im(\omega_R t + \gamma^{ij})} \left[\frac{3}{2\sqrt{6}} \sum_{i \neq j} b_{ij} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij} \right] \right) * \\ &\quad * \left(\frac{1}{4\sqrt{6}} [-C_1^{ij} (\alpha^{ij}, \beta^{ij}) e^{-i\gamma^{ij}} \left(\frac{1}{2i\omega_R} \right) (e^{2i\omega_R t} - 1)] \right) dt \\ &+ \int_0^{\tau_R} \left(\sum_{m=-\infty}^{+\infty} e^{-im(\omega_R t + \gamma^{ij})} \left[\frac{3}{2\sqrt{6}} \sum_{i \neq j} b_{ij} \sum_{n=-2}^{+2} a_{m-n} C_n^{ij} \right] \right) * \\ &\quad * \left(\frac{1}{4\sqrt{6}} [C_{-1}^{ij} (\alpha^{ij}, \beta^{ij}) e^{-i\gamma^{ij}} \left(\frac{1}{2i\omega_R} \right) (e^{2i\omega_R t} - 1)] \right) dt \\ &= 0 \end{aligned} \quad (158)$$

A2. Table of Wigner d-matrix Elements for $j = 1$ and $j = 2$

$$d_{m' m}^j = (-1)^{m-m'} d_{mm'}^j, \quad (159)$$

$$d_{0,0}^2(\beta) = \frac{3\cos^2(\beta) - 1}{2}, \quad (160)$$

$$d_{0,\pm 2}^2(\beta) = \sqrt{\frac{3}{8}} \sin^2(\beta), \quad (161)$$

$$d_{0,\pm 1}^2(\beta) = \pm \sqrt{\frac{3}{8}} \sin(2\beta), \quad (162)$$

$$d_{20}^2(-\beta_{rf}) = \sqrt{\frac{3}{8}} \sin^2(\beta_{rf}), \quad (163)$$

$$d_{1,0}^2(\beta_{RL}) = -d_{01}^2(\beta_{RL}) = -\sqrt{\frac{3}{8}} \sin(2\beta_{RL}), \quad (164)$$

$$d_{1,\pm 1}^2(\beta) = \frac{1 \pm \cos(\beta)}{2} (2\cos(\beta) \mp 1) \quad (165)$$

$$d_{2,\pm 1}^2(\beta) = \frac{1 \pm \cos(\beta)}{2} \sin(\beta) \quad (166)$$

$$d_{2,\pm 2}^2(\beta) = \left(\frac{1 \pm \cos(\beta)}{2} \right)^2 \quad (167)$$

A3

a- Second-Rank Spherical Harmonics

$$Y_{2\pm 2} = \frac{1}{2} \sin^2\Theta e^{\pm 2i\Phi}, \quad (168)$$

$$Y_{2\pm 1} = -(\pm \sin\Theta \cos\Theta e^{\pm i\Phi}), \quad (169)$$

$$Y_{20} = \frac{1}{\sqrt{6}} (3\cos^2\Theta - 1) \quad (170)$$

b- Explicit Expressions of The Coefficients $C_n^{\hat{1}j}$

$$C_n^{ij}(\alpha^{ij}, \beta^{ij}) = d_{0,n}^2(\theta_M) \sum_{n'=-2}^2 (-1)^{n'} Y_{2n'}^{ij} e^{-in\alpha^{ij}} d_{n-n'}^2(\beta^{ij}) \\ = d_{0,n}^2(\theta_M) [Y_{2-2}^{ij} e^{-in\alpha^{ij}} d_{n,2}^2(\beta^{ij}) - Y_{2-1}^{ij} e^{-in\alpha^{ij}} d_{n,1}^2(\beta^{ij}) + Y_{20}^{ij} e^{-in\alpha^{ij}} d_{n,0}^2(\beta^{ij})] \quad (171) \\ + d_{0,n}^2(\theta_M) [-Y_{21}^{ij} e^{-in\alpha^{ij}} d_{n,-1}^2(\beta^{ij}) + Y_{22}^{ij} e^{-in\alpha^{ij}} d_{n,-2}^2(\beta^{ij})]$$

$$C_1^{ij}(\alpha^{ij}, \beta^{ij}) = \frac{1}{\sqrt{3}} e^{-i\alpha^{ij}} [Y_{2-2}^{ij} d_{1,2}^2(\beta^{ij}) - Y_{2-1}^{ij} d_{1,1}^2(\beta^{ij}) + Y_{20}^{ij} d_{1,0}^2(\beta^{ij}) - Y_{21}^{ij} d_{1,-1}^2(\beta^{ij}) + Y_{22}^{ij} d_{1,-2}^2(\beta^{ij})] \quad (172)$$

$$C_2^{ij}(\alpha^{ij}, \beta^{ij}) = \frac{1}{\sqrt{6}} e^{-i\alpha^{ij}} [Y_{2-2}^{ij} d_{2,2}^2(\beta^{ij}) - Y_{2-1}^{ij} d_{2,1}^2(\beta^{ij}) + Y_{20}^{ij} d_{2,0}^2(\beta^{ij}) - Y_{21}^{ij} d_{2,-1}^2(\beta^{ij}) + Y_{22}^{ij} d_{2,-2}^2(\beta^{ij})] \quad (173)$$

A4. CALCULATION OF THE MAGNITUDES

a- The Magnitude of the C7 average Hamiltonian

$$\left| \overline{H}_{DQ}^0 \right|_{C7} = \frac{343}{520\pi\sqrt{2}} |e^{i\frac{\pi}{14}} + i| b_{ij} \sin(2\beta_{PR}) \\ = \frac{1}{7} \frac{343}{520\pi} \sqrt{1 + \sin(\frac{\pi}{14})} b_{ij} \sin(2\beta_{PR}) \quad (174) \\ = 0.040 b_{ij} \sin(2\beta_{PR})$$

b- The Magnitude of the BABA average Hamiltonian using only the central term corresponding to $n' = 0$

$$\left| \overline{H}_{DQ}^0 \right|_{BABA} = \frac{3}{2\sqrt{6}\pi} \frac{1}{2\sqrt{2}} Y_{20} b_{ij} \sin(\gamma^{ij}) \sin(2\beta_{PR}) \quad (175)$$

For a particular direction of the internuclear vector in polar coordinates in the laboratory axis system corresponding for example to $\Theta = 0$, and $Y_{20} = \frac{2}{\sqrt{6}}$, we have

$$\left| \overline{H}_{DQ}^0 \right|_{BABA} = \frac{3}{2\sqrt{6}\pi} \frac{1}{2\sqrt{2}} \frac{2}{\sqrt{6}} Y_{20} b_{ij} \sin(\gamma^{ij}) \sin(2\beta_{PR}) \simeq 0.056 b_{ij} \sin(\gamma^{ij}) \sin(2\beta_{PR}) \quad (176)$$

c- The Magnitude of the BABA2 average Hamiltonian using only the central term corresponding to $n' = 0$

$$\begin{aligned}
 \left| \overline{H}_{DQ}^0 \right|_{BABA2} &= \frac{3}{2\sqrt{6\pi}} \frac{1}{\sqrt{6}} Y_{20}^{ij} d_{20}^2(\beta^{ij}) b_{ij} \\
 &= \frac{3}{2\sqrt{6\pi}} \frac{1}{\sqrt{6}} Y_{20}^{ij} \frac{\sqrt{6}}{4} b_{ij} \sin(\gamma^{ij}) \sin^2(\beta^{ij}) \quad (177) \\
 &= \frac{3}{8\sqrt{6\pi}} Y_{20}^{ij} b_{ij} \sin(\gamma^{ij}) \sin^2(\beta^{ij})
 \end{aligned}$$

Fig. 1.
BABA Pulse Sequence

Fig. 2.
BABA2 Pulse Sequence

Fig. 3.
C7 Pulse Sequence

Fig. 4a **Fig. 4b** **Fig. 4c** **Fig. 4.**

Fig. 5.