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Applications of Floquet-Magnus expansion, average Hamiltonian theory and Fer expansion to study interactions in solid state NMR when irradiated with the magic-echo sequence

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Abstract

This work presents the possibility of applying the Floquet-Magnus expansion and the Fer expansion approaches to the most useful interactions known in solid-state nuclear magnetic resonance using the magic-echo scheme. The results of the effective Hamiltonians of these theories and average Hamiltonian theory are presented.

I. Introduction

With the continued increase in the complexity of nuclear magnetic resonance (NMR) techniques and applications, theory of spin dynamics has become an indispensable part of modern day research. Theoretical approaches are now commonly used for designing sophisticated pulse sequences, numerical simulations of NMR experiments, and understanding new experiments. This is especially true for solid-state NMR, where spectra are very broad due to full effects of anisotropic or orientation-dependent interactions. A number of special techniques and equipment, including magic angle spinning (MAS), cross polarization, special 2D experiments, enhanced probe electronics, etc, are used in solid-state NMR to obtain high resolution spectra. Indeed, the presence of broad NMR lineshapes, once thought to be a hindrance, actually provides much information on chemistry, structure and dynamics in solid state.

In this article, we applied a well-known theory and two promising theories that can be useful to study interactions in the static and rotating samples (MAS) when irradiated with multiple pulse sequences such as magic-echo pulse sequence. The magic echo sequence has been applied with great success in solid state NMR. While the well-known theory of average Hamiltonian theory (AHT)⁴ is a powerful analytical tool, it is not always applicable or sufficiently accurate. The technique of AHT is more appropriated for static experiments and stroboscopic observation, and has been used to study all types of interactions encountered in

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NMR, such as chemical shift anisotropy⁹⁻¹¹, dipolar^{9,10,12}, and quadrupolar^{11,13,14} interactions. While this technique remains the most popular theoretical technique used so far in NMR because of its intuitive way of obtaining effective time-independent Hamiltonians, it is limited to a single time-dependent perturbation¹⁵. Driven by demands of the experimental NMR, Floquet theory (FLT)⁵⁻⁸ was introduced nearly three decades ago to the NMR community for describing the spin dynamics at all times. This approach is appropriated for rotating experiments, and can also be used to study all types of interactions encountered in NMR, such as those investigated in this paper. The FLT will be the subject of our forthcoming article and its investigation has not been studied or included in this article. Instead, in this paper we studied Floquet-Magnus expansion (FME)^{1,2,26,27} which is an alternative and unique approach in spin dynamics that shed new lights on both, AHT and FLT. This new scheme (FME), recently introduced to the solid-state NMR community had only been applied to Zeeman³¹ and dipolar^{22,23} interactions, and can be applied to any NMR interactions such as those investigated in this work.

Another approach we studied in this paper is the Fer expansion (FE)^{24,28}, recently introduced to the NMR community. The Fer expansion²⁴ was illustrated in NMR by considering simple applications in the calculation of Bloch-Siegert shift in NMR and analyzing heteronuclear decoupling²¹ in solid-state NMR. The difference between the Magnus (AHT) and Fer expansions lies in the form of the correction terms. In this work, we calculated the first order term of the Fer expansion scheme using the standard Hamiltonians previously investigated with the method of AHT. We presented some connections between the Fer expansion and the AHT (Magnus expansion).

The ultimate goal of this article is to show the potential and the applicability that each theory therein offers to different interactions in NMR. We presented the results of effective Hamiltonians of each of these theories in practical cases. The paper is organized as follows: the next section summarizes the essential theoretical background information for the AHT, FME, and FE. The sub-section II. 4 shows a table of useful theories as well as their introduced date in the field of solid-state NMR. Section III describes various interactions in solid-state NMR. The applications of the aforementioned three theories (AHT, FME, and FE) to the chemical shift anisotropy (CSA), dipolar, and quadrupolar interactions when irradiated with the magic echo pulse sequence is presented in the sub-section IV. Finally, section V and VI of the paper discusses and summarizes our conclusions, respectively.

II. Theoretical Background

II. 1. Average Hamiltonian Theory⁴

The formalism used in the technique of AHT can be described as following: the time evolution of the system, from the initial state ($t=0$, $\rho(0)$) to the state at time $t=t_c$, $\rho(t_c)$, is given by

$$\rho(t_c) = U_{RF} U_{int} \rho(0) U_{int}^{-1} U_{RF}^{-1} \quad (1)$$

where the propagator U_{RF} is given by the Dyson series

$$U_{RF} = \dots U_2 U_1 U_0 \quad (2)$$

and U_{int} is given by the Magnus expansion

$$U_{\text{int}}(t, 0) = \exp \left[-it_c \left(\overline{H}_{\text{int}}^0 + \overline{H}_{\text{int}}^1 + \dots \right) \right] \quad (3)$$

with

$$\overline{H}_{\text{int}}^0 = \frac{1}{t_c} \int_0^{t_c} \tilde{H}_{\text{int}}(\tau) d\tau, \quad (4)$$

$$\overline{H}_{\text{int}}^1 = \frac{-it_c}{2t_c} \int_0^{t_c} \left[\tilde{H}_{\text{int}}(\tau), \int_0^{\tau} \tilde{H}_{\text{int}}(\phi) d\phi \right] d\tau, \quad (5)$$

$$\overline{H}_{\text{int}}^2 = \dots \quad (6)$$

The operator U_{RF} represents the interaction associated with the sequence of RF pulses applied over a time t_c , and H_{int} refers to the systems' internal Hamiltonian. An attractive feature of AHT is that, a variety of Hamiltonians can be accounted for in the system evolution including pulse errors and finite pulse width effects¹³.

II. 2. Floquet-Magnus Expansion^{2,26,27}

The Floquet-Magnus expansion is a new theoretical tool for describing spin dynamics in of solid state NMR experiments. This approach (FME) is an extension of the popular Magnus Expansion and Average Hamiltonian Theory. Calculations with the FME can be performed in a finite-dimensional Hilbert space instead of an infinite dimensional space within the Floquet theory described in the articles^{2,6,7,8}.

Considering the initial conditions to be $\Lambda(0) = 0$ (i.e., $R(0) = I$), Blanes et al.^{26,27} derived explicitly, the following equations²²:

$$\Lambda_1(t) = \int_0^t H(x) dx - tF_1, \quad (7)$$

$$F_1 = \frac{1}{T} \int_0^T H(x) dx, \quad (8)$$

$$\Lambda_2(t) = \frac{1}{2} \int_0^t [H(x) + F_1, \Lambda_1(x)] dx - tF_2, \quad (9)$$

$$F_2 = \frac{1}{2T} \int_0^T [H(x) + F_1, \Lambda_1(x)] dx, \quad (10)$$

$$\Lambda_3(t) = \frac{i}{2} \int_0^t \{[\Lambda_2, H + F_1] + [\Lambda_1, F_2]\} dx - \frac{1}{12} \int_0^t \{[\Lambda_1, [\Lambda_1, H - F_1]]\} dx - tF_3 \quad (11)$$

$$F_3 = \frac{i}{2T} \int_0^T \{[\Lambda_2, H + F_1] + [\Lambda_1, F_2]\} dx - \frac{1}{12T} \int_0^T \{[\Lambda_1, [\Lambda_1, H - F_1]]\} dx - tF_3 \quad (12)$$

The above equations are now considered to be a particular case ($\Lambda(0) = 0$) of a more general representation of the FME² with $\Lambda(0) \neq 0$. The general formula for the contribution of the FME is given by

$$\Lambda_n(t) = \Lambda_n(0) + \int_0^t G_n(x) dx - tF_n, \quad (13)$$

with

$$F_n = \frac{1}{T} \int_0^T G_n(x) dx. \quad (14)$$

The first order contributions to the FME give explicitly

$$G_1(x) = H(x), \quad (15)$$

$$G_2(x) = -\frac{i}{2} [H(x) + F_1, \Lambda_1(x)], \quad (16)$$

$$G_3(x) = -\frac{i}{2} [H(x) + F_1, \Lambda_2(x)] - \frac{i}{2} [F_2, \Lambda_1(x)] - \frac{1}{12} [\Lambda_1(x) [\Lambda_1(x), H(x) - F_1]] \quad (17)$$

Symbolic calculations software can enable formal derivation of higher order terms. In the above equations (Eqs. (11-21)), the $\Lambda_n(t)$ functions with $n = 1, 2, 3, \dots$, represents the n^{th} order term of the argument of the operator that introduces the frame such that the spin system operator is varying under the time independent Hamiltonian F . The $\Lambda_n(t)$ functions can be useful to quantify the level of productivity of double quantum terms such as in the article²².

II. 3. Fer Expansion^{24,28}

The formalism of Fer expansion expresses the solution to the differential time-dependent Schrodinger equation in the form of an infinite-product of a series of exponentials as following

$$U(t) = \prod_{k=1}^{\infty} e^{F_k(t)} = e^{F_1(t)} e^{F_2(t)} \dots \quad (18)$$

A knowledge of the Hamiltonian allow an easy evaluation of

$$F_1 = \int_0^t dt' H(t') \quad (19)$$

and

$$H_F^1 = e^{-F_1(t)} H e^{F_1(t)} - \int_0^1 dx e^{-xF_1(t)} H e^{xF_1(t)}. \quad (20)$$

The following iterative formula were derived^{24,28}

$$F_n = -i^n \int_0^t dt' H_F^{(n-1)}(t'), \quad H_F^{(0)} = H, \quad (21)$$

$$H_F^{(n)} = -\frac{1}{2} [F_n, H_F^{(n-1)}] + \frac{1}{3} [F_n, [F_n, H_F^{(n-1)}]] + \dots \quad (22)$$

where $n = 1, 2, 3, \dots$. The form of Eq. (22) shows that the Fer expansion generates a series of nested commutators involved in the calculation of $H_F^{(n)}$. The Fer expansion differs to the Magnus approach in the form of the correction terms.

II. 4. Some Literature Examples of Theories in Solid State NMR

The following Table 1 includes some useful theories in solid-state NMR, as well as their introduced date in the field of NMR.

III. Various Interactions in Solid-State Nuclear Magnetic Resonance

The interactions of spin systems in NMR have been extensively described by Levitt²⁹, Veshtort and Griffin³⁰, and Bak et al³¹. In this part of the paper, we summarized the various forms of Hamiltonians subject to the secular approximation of high-field truncation. The Hamiltonian of the spin system is the sum of the different physical influence or interaction acting on the nuclear spin such as the chemical shift, dipole-dipole coupling, or quadrupolar coupling. Mathematically, the spin Hamiltonian in NMR can be written as

$$H = \sum_{\Lambda} H^{\Lambda}, \quad (23)$$

where Λ represents the contributions from radiofrequency (RF) irradiation, chemical shift (CS), indirect spin-spin coupling (J), dipole-dipole coupling (D), quadrupolar coupling (Q) and so on. In general, the interactions of the nuclei with the excitation field (external radiation) and the internal Hamiltonians (CS, J, D, Q) do not commute.

In high magnetic field NMR, all interaction terms have the spin quantum numbers equal to zero ($\mu = 0, m = 0$), and the spin Hamiltonians are truncated by the secular approximation. The NMR interactions are written explicitly by the following expressions³¹

$$H_{RF} = \sum_i \left| \omega_{RF}^i(t) \right| (I_{ix} \cos \phi_i + I_{iy} \sin \phi_i), \quad (24)$$

$$H_{CS} = \sum_i \omega_{CS,0}^i(t) I_{iz}, \quad (25)$$

$$H_J = \sum_{ij} -\omega_{J_{iso},0}^{ij}(t) \frac{1}{\sqrt{3}} \mathbf{I}_i \cdot \mathbf{I}_j + \omega_{J_{aniso},0}^{ij}(t) \frac{1}{\sqrt{6}} (3I_{iz}I_{jz} - \mathbf{I}_i \cdot \mathbf{I}_j), \quad (26)$$

$$H_D = \sum_{i,j} \omega_{D,0}^{ij}(t) \frac{1}{\sqrt{6}} (3I_{iz}I_{jz} - \mathbf{I}_i \cdot \mathbf{I}_j), \quad (27)$$

$$H_Q = \sum_i \omega_{Q,0}^i(t) \frac{1}{\sqrt{6}} \left(3I_{iz}^2 - I_i^2 \right) + \frac{1}{2\omega_0^i} \left\{ \omega_{Q,-2}^i(t) \omega_{Q,2}^i(t) \left(2I_i^2 - 2I_{iz}^2 - 1 \right) I_{iz} \right. \\ \left. + \omega_{Q,-1}^i(t) \omega_{Q,1}^i(t) \left(4I_i^2 - 8I_{iz}^2 - 1 \right) I_{iz} \right\}, \quad (28)$$

with i, j representing the concerned spins. ϕ_j is the phase of the RF irradiation (pulse phases), and $\omega_i^{RF} = -\gamma_i B_{RF}^i$ is the RF nutation frequency. (CS) represents the chemical shift, (J) is the indirect spin-spin coupling, (D) represents the dipole-dipole coupling, and (Q) is the quadrupolar coupling. The symbols γ_i is the gyromagnetic ratio, and J_{iso} and J_{aniso} describe scalar and anisotropic J coupling, respectively. Details on the above NMR interactions (Eqs. (24-28)) can be found in the literature^{25,29-31,37-40}.

The operator product $I_i I_j$ is truncated to $I_{iz} I_{jz}$ when a coupling occurs between nuclei of different spin species. In the Eq. (28), the first term represents the first-order quadrupolar coupling while the second terms include the secular components for the second-order quadrupolar coupling. In the following, we have neglected the second-order term with the secular components. The Eq. (28) is reduced to

$$H_Q = \sum_i \omega_{Q,0}^i(t) \frac{1}{\sqrt{6}} \left(3I_{iz}^2 - I_i^2 \right). \quad (29)$$

The frequency coefficients for the various internal Hamiltonians depend on some physical parameters and are typically expressed in terms of Fourier expansion such as

$$\omega_{\lambda,m'}(t) = \sum_{m=-2}^2 \omega_{\lambda,m'}^{(m)} e^{im\omega_r t} \quad (30)$$

where $\frac{\omega_r}{2\pi}$ is the spin rate. The Fourier coefficients are written as

$$\omega_{\lambda,m'}^{(m)} = \omega_{iso}^\lambda \delta_{m,0} + \omega_{aniso}^\lambda \left\{ D_{0,-m}^{(2)} \left(\Omega_{PR}^\lambda \right) - \frac{\eta^\lambda}{\sqrt{6}} \left[D_{-2,-m}^{(2)} \left(\Omega_{PR}^\lambda \right) + D_{2,-m}^{(2)} \left(\Omega_{PR}^\lambda \right) \right] \right\} d_{-m,m'}^{(2)}(\beta_{RL}) \quad (31)$$

where $\delta_{m,0}$ is the standard Kronecker delta. The constants describing the isotropic (ω_{iso}^λ), and the anisotropic ($\omega_{aniso}^\lambda, \eta^\lambda$) contributions to the Fourier coefficients can be found in the article by Bak et al.³¹. The article also gives a description of the orientation dependence for the anisotropic interactions. The frames P, R, C, and L represent the principal-axis, the rotor-fixed, the crystal-fixed, and the laboratory-fixed frames, respectively. These frames (P, R, S, and L) are connected by the relation

$$D_{m',m}^{(2)}(\Omega_{PR}^\lambda) = \sum_{m''=-2}^2 D_{m',m''}^{(2)}(\Omega_{PC}^\lambda) D_{m'',m}^{(2)}(\Omega_{CR}). \quad (32)$$

The internal Hamiltonians (Eqs. (24)-(28)) can also be written in more succinct forms such as those described by Tycko³² or Schnell and Spiess²⁵. For instance, in the form given by Tycko, the Hamiltonian is expressed in terms of $\{Y_{2m}\}$ which is a basis for an irreducible representation of rotations of the spatial coordinates of the sample, and $\{T_{2m}\}$ which is a basis for an irreducible representation of rotations of the spin angular momenta. $\{Y_{2m}\}$ and $\{T_{2m}\}$ are second-rank spherical harmonics, and second-rank irreducible tensor operators, respectively. In high field approximation, we only have the two basis $\{Y_{20}\}$ and $\{T_{20}\}$. For example, the truncated dipole-dipole coupling can be written as

$$H_D = b_{ij} Y_{20} T_{20} \quad (33)$$

where b_{ij} is the coupling constant proportional to r_{ij}^{-3} (and r_{ij} is the internuclear distance). The quadrupolar interaction can also be written as

$$H_Q^{(0)}(t) = \sum_{m=-2}^2 \left\{ \frac{1}{\sqrt{6}} D_{m0}^{(2)}(\Omega) + \eta \left[D_{m2}^{(2)}(\Omega) + D_{m-2}^{(2)}(\Omega) \right] \right\} D_{0m}^{(2)}[\Omega'(t)] T_{20}. \quad (34)$$

where η is the asymmetry parameter.

IV. Applications

The magic echo sequence (Fig. 1) is a multiple pulse sequence that has been applied with great success in solid state NMR. The scheme consists of a period of free evolution of time $\tau - \alpha$, a $\frac{\pi}{2}$ pulse about the y axis, followed by two spin locking fields of duration $2\tau - \alpha$, and ending with the application of a second $\frac{\pi}{2}$ pulse about the y axis. The cycle is well known in the NMR community to be more efficient than a simple two-pulse quadrupolar echo (solid echo) sequence (Fig. 2). Specifically, sufficient line-narrowing may be obtained for the magic echo sequence when the free evolution times are made long enough (i.e., μ s to 10s). This is in contrast to quadrupolar echo sequence where efficient line-narrowing is obtained when using very short free evolution times (typically less than 10 μ s). This characteristic can be explained by considering the convergence of the Magnus expansion with strong RF

power and short pulse spacings. The Magnus expansion converges faster with the magic echo sequence compared to the conventional two-pulse quadrupolar echo cycle as in the article by Mananga et al.¹¹. More details on the efficiency of the magic echo cycle compared to the simple two-pulse quadrupolar echo sequence can be found in the literature of solid-state NMR spectroscopy^{9,10,11,34,35,36}. Fig. 3 also represents the magic echo sequence for refocusing the quadrupolar interaction. In the following subsections, we investigated various interactions in the solid-state when samples are irradiated using the magic echo pulse

sequence. We have neglected J coupling in this paper and all the duration of the $\frac{\pi}{2}$ pulses are 2α . We consider only the first-order quadrupolar coupling and neglect all the secular components from the second and upper-order.

IV. 1. Using Average Hamiltonian Theory

We consider the static case where the AHT is more convenient to study the spin dynamics. The zero-order term of the average Hamiltonian was calculated with the magic echo pulse sequence for each interaction^{9,11}:

$$\bar{H}_{\Delta\omega}^0 = \frac{1}{3\tau} \frac{\Delta\omega}{\omega_{RF}} I_y [1 - \cos \omega_{RF} (2\tau - \alpha)] - \frac{1}{3\tau} \frac{\Delta\omega}{\omega_{RF}} I_x \left[\sin \omega_{RF} (2\tau - \alpha) + \frac{4}{\pi} \omega_{RF} \alpha \right] \quad (35)$$

$$\begin{aligned} \bar{H}_D^0 = & \omega_D I_z I_z \\ & - \omega_D I.I \\ & + \frac{1}{4\tau} \frac{\omega_D}{\omega_{RF}} I_x I_x [2\omega_{RF} (2\tau - \alpha) \\ & + \alpha] \\ & + \sin 2\omega_{RF} (2\tau - \alpha) \\ & + \frac{1}{4\tau} \frac{\omega_D}{\omega_{RF}} I_y I_y [2\omega_{RF} (2\tau - \alpha)] - \sin 2\omega_{RF} (2\tau - \alpha) \\ & - \frac{1}{2\tau} \frac{\omega_D}{\omega_{RF}} [I_x I_y \\ & + I_y I_x] \sin^2 \omega_{RF} (2\tau - \alpha) \end{aligned} \quad (36)$$

$$\bar{H}_{\omega_Q}^0 = \frac{1}{7\tau} \frac{12\alpha\omega_Q}{\pi} I_{x,2} + \frac{4(3\alpha - \tau)\omega_Q}{7\tau} [I_{x,1} I_{x,1} + I_{y,1} I_{y,1} - 2I_{z,1} I_{z,1}] \quad (37)$$

where 2α is the duration of $\pi/2$ pulse width, and ω_D is the dipolar coupling constant. ω_{RF} is the RF field strength, ω is the resonance offset, and ω_Q is the quadrupolar coupling constant. The sequence used for the chemical shift and the dipolar interactions consists of a

period of free evolution of time $\tau - \alpha$, a $\frac{\pi}{2}$ pulse about the y axis, followed by two spin

locking fields of duration $2\tau - \alpha$, and ending with the application of a second $\frac{\pi}{2}$ pulse about the y axis. The echo occurs at a time $\tau - \alpha$ after the last pulse. For the sequence used in the

case of the quadrupolar interaction, a $\frac{\pi}{2}$ pulse about the x axis precedes the magic echo sequence. In the expression of the average Hamiltonian obtained for the quadrupolar interaction, the spin-1 operator formalism developed by Vega and Pines³³ has been used. Note that, the zero-order term of the average Hamiltonian for the quadrupolar interaction

(Eq. 37) is obtained when using the magic echo sequence with a $\frac{\pi}{2}$ pulse about the x axis inserted during the first free evolution time as in the figure showed in the previous work by Mananga et al.¹¹.

IV. 2. Using Fer Expansion

For the Fer expansion, a direct integration of the toggling frames of the various Hamiltonians described above lead to the expression of $F_1(t)$. The following results are obtained for the chemical shift, dipolar and quadrupolar interactions.

$$F_{1(CS)}(t) = \frac{2\Delta\omega}{\omega_{RF}} I_x (\cos \omega_{RF} t - 1) + \frac{\Delta\omega}{\omega_{RF}} \left[-I_x (\sin \omega_{RF} t + \sin \omega_{RF} (t - \xi) + \sin \omega_{RF} \xi) \right. \\ \left. + I_y (-\cos \omega_{RF} t + 1 - \cos \omega_{RF} (t - \xi) + \cos \omega_{RF} \xi) \right] \quad (38)$$

$$F_{1(D)} = 2\omega_D (3I_z I_z - \mathbf{I} \cdot \mathbf{I}) t + \frac{\omega_D}{\omega_{RF}} \left\{ 3I_z I_z \left(\frac{1}{2} \sin 2\omega_{RF} t + \omega_{RF} t \right) \right. \\ + I_x I_x \left(-\frac{1}{2} \sin 2\omega_{RF} t + \omega_{RF} t \right) - 4\omega_{RF} \mathbf{I} \cdot \mathbf{I} t + \frac{3}{2} I_x I_x \left(\frac{1}{2} \sin 2\omega_{RF} t + \omega_{RF} t \right) \\ + \frac{1}{2} \sin 2\omega_{RF} (t - \xi) + \omega_{RF} (t - \xi) \Big) + \\ + \frac{3}{2} I_y I_y \left(-\frac{1}{2} \sin 2\omega_{RF} t + \omega_{RF} t - \frac{1}{2} \sin 2\omega_{RF} (t - \xi) + \omega_{RF} (t - \xi) \right) - \\ \left. \frac{3}{4} (I_x I_y + I_y I_x) (\cos 2\omega_{RF} t + \cos 2\omega_{RF} (t - \xi)) \right\} \quad (39)$$

$$\begin{aligned}
F_{1(Q)} = & \omega_Q (12I_{z,1}I_{z,1} + 24I_{y,1}I_{y,1} - 9I_x) t + \frac{\omega_Q}{2\omega_{RF}} \{ (12I_{z,1}I_{z,1} + 12I_{y,1}I_{y,1} + 24I_{x,1}I_{x,1}) \\
& \left(\frac{1}{2} \sin 2\omega_{RF} t + \omega_{RF} t \right) + (12I_{z,1}I_{z,1} + 24I_{y,1}I_{y,1} \\
& + 12I_{x,1}I_{x,1} \left(-\frac{1}{2} \sin 2\omega_{RF} t + \omega_{RF} t \right) + 12I_{x,1}I_{x,1} \left(\frac{1}{2} \sin 2\omega_{RF} (t - \xi) \right. \\
& \left. + \omega_{RF} (t - \xi) \right) + 12I_{z,1}I_{z,1} \left(-\frac{1}{2} \sin 2\omega_{RF} (t - \xi) + \omega_{RF} (t - \xi) \right) - 6(I_{y,2} + I_{z,2}) \cos 2\omega_{RF} t + 6I_{y,2} \cos 2\omega_{RF} (t - \xi) \} \\
\end{aligned} \tag{40}$$

where

$$\xi = 2\tau - \alpha. \tag{41}$$

To proceed further, $H_F^{(1)}$ needs to be calculated using the value of $F_1(t)$. We have for the first two orders:

$$H_F^{(1)} = -\frac{1}{2} [F_1, H_F^0] + \frac{1}{3} \{F_1^2, H_F^0\} \tag{42-a}$$

which can also be written as

$$H_F^{(1)} = -\frac{1}{2} [F_1, H_F^0] + \frac{1}{3} [F_1, [F_1, H_F^0]]. \tag{42-b}$$

The iteration process can continue easily when the initial values of $F_n(t)$ and $H_F^{(n)}$ are found.

IV. 3. Using Floquet-Magnus Expansion

In this subsection, we used the FME under the combined presence of MAS and RF irradiation, with their cycle times being non-commensurate. Let us consider the following representation that governs the free evolution time in the magic echo pulse sequence:

In Fig. 4, the time-dependent function $\theta(t)$ can be expressed in the form of the Fourier expression

$$\theta(t) = \sum_{k=-\infty}^{+\infty} a_k \exp(-ik\omega_R t), \tag{43}$$

with a_k representing the time-independent Fourier coefficients corresponding to the Fourier index k . The coefficients a_k are obtained by

$$a_k = \frac{1}{\tau_R} \int_0^{\tau_R} \theta(t) e^{ik\omega_R t} dt. \quad (44)$$

The coefficients in the first part of the sequence are

$$a_k^{(1)} = \frac{1}{\tau_R} \int_0^{\tau-\alpha} e^{ik\omega_R t} dt \quad (45)$$

which are given explicitly by

$$a_0^{(1)} = \frac{1}{\tau_R} \int_0^{\tau-\alpha} dt = \frac{\tau - \alpha}{\tau_R}, \quad (46)$$

and

$$a_k^{(1)} = \frac{1}{2\pi ik} \left[e^{ik2\pi \left(\frac{\tau-\alpha}{\tau_R} \right)} - 1 \right], \quad (\text{for } k \neq 0), \quad (47)$$

with

$$\omega_R = \frac{2\pi}{\tau_R}. \quad (48)$$

In the second part of the sequence, we have

$$a_k^{(2)} = \frac{1}{\tau_R} \int_{5\tau+\alpha}^{6\tau} e^{ik\omega_R t} dt. \quad (49)$$

This can also be written explicitly by

$$a_0^{(2)} = \frac{1}{\tau_R} \int_{5\tau+\alpha}^{6\tau} dt = \frac{\tau - \alpha}{\tau_R}, \quad (50)$$

and

$$a_0^{(2)} = \frac{1}{2\pi ik} \left[e^{ik12\pi\left(\frac{\tau}{\tau_R}\right)} - e^{ik2\pi\left(\frac{5\tau+\alpha}{\tau_R}\right)} \right], \text{ (for } k \neq 0). \quad (51)$$

The Eq. (51) can be arranged as

$$a_k^{(2)} = \frac{1}{2\pi ik} e^{ik2\pi\left(\frac{5\tau+\alpha}{\tau_R}\right)} \left[e^{ik2\pi\left(\frac{\tau-\alpha}{\tau_R}\right)} - 1 \right]. \quad (52)$$

Globally, we have

$$a_0^{(1)} = a_0^{(2)} = \frac{\tau - \alpha}{\tau_R} = a_0, \quad (53)$$

$$a_k^{(2)} = a_k^{(1)} e^{ik2\pi\left(\frac{5\tau+\alpha}{\tau_R}\right)} = a_k. \quad (54)$$

If we set

$$\phi = \frac{\alpha}{\tau_R}, \quad (55)$$

and

$$\tau = c\tau_R, \quad (56)$$

where c is a constant, and the criterion

$$a_0 = c - \phi. \quad (57)$$

The coefficients a_k can be rewritten

$$a_k = a_k^{(1)} e^{ik2\pi(5c+\phi)} = \frac{1}{2\pi ik} \left[e^{ik2\pi(c-\phi)} - 1 \right] e^{ik2\pi(5c+\phi)}. \quad (58)$$

These equations could be helpful to control the free evolution times as well as the finite pulse width effects during the optimizations of experiments. In this new picture, the toggling frame is written as

$$\tilde{H}_{\lambda}(t) = \tilde{H}_{(1)}\theta(t) + \tilde{H}_{(2)} + \tilde{H}_{(3)} + \tilde{H}_{(4)} + \tilde{H}_{(5)} + \tilde{H}_{(6)}(1 - \theta(t)) \quad (59)$$

where λ represents the various internal Hamiltonians investigated in this paper, i.e. $\lambda = \text{CS}$, D, and Q. The terms $\tilde{H}_{(1)}$, $\tilde{H}_{(2)}$, $\tilde{H}_{(3)}$, $\tilde{H}_{(4)}$, $\tilde{H}_{(5)}$ and $\tilde{H}_{(6)}$ represent the toggling frame dipolar Hamiltonians⁹. The resulting first-order terms of the various interactions in the FME are calculated using Eqs. (7) and (8). Details of calculations are given in the appendix.

For Chemical Shift (CS)—

$$F_{1(\text{CS})} = \bar{H}_{\Delta\omega}^0 = \frac{1}{3\tau} \frac{\Delta\omega}{\omega_{\text{RF}}} I_y [1 - \cos \omega_{\text{RF}} (2\tau - \alpha)] - \frac{1}{3\tau} \frac{\Delta\omega}{\omega_{\text{RF}}} I_x \left[\sin \omega_{\text{RF}} (2\tau - \alpha) + \frac{4}{\pi} \omega_{\text{RF}} \alpha \right] \quad (60)$$

$$\begin{aligned} \Lambda_{1(\text{CS})}(t) = & \sum_{n=-2}^{+2} C_n \left[-(I_A + 2I_B + I_C) I_x + (I_B + I_D) I_y + \left(\frac{1}{in\omega_R} \right) (e^{-in\omega_R t} - 1) (1 - 2a_0) \right. \\ & \left. + \sum_{m=-\infty}^{\infty} \left(\frac{-2}{im\omega_R} \right) a_{m-n} (e^{-im\omega_R t} - 1) \right] I_z - tF_{1(\text{CS})} \end{aligned} \quad (61)$$

where I_A , I_B , I_C and I_D are given by:

$$\begin{aligned} I_A = & \int_0^t e^{-in\omega_R t'} \cos(\omega_{\text{RF}} t') dt' \\ = & \frac{1}{(n^2\omega_R^2 - \omega_{\text{RF}}^2)} [-in\omega_R + in\omega_R \exp(-in\omega_R t) \cos(\omega_{\text{RF}} t) + -\omega_{\text{RF}} \exp(-in\omega_R t) \sin(\omega_{\text{RF}} t)] \end{aligned} \quad (62)$$

$$\begin{aligned}
 I_B &= \int_0^t e^{-in\omega_R t'} \sin(\omega_{RF} t') dt' \\
 &= \frac{1}{(n^2 \omega_R^2 - \omega_{RF}^2)} [-\omega_{RF} + \omega_{RF} \exp(-in\omega_R t) \cos(\omega_{RF} t) + in\omega_R \exp(-in\omega_R t) \sin(\omega_{RF} t)]
 \end{aligned}
 \tag{63}$$

$$\begin{aligned}
 I_C &= \int_0^t e^{-in\omega_R t'} \cos \omega_{RF} (t' - \xi) dt' = -\frac{1}{(n^2 \omega_R^2 - \omega_{RF}^2)} [in\omega_R \cos(\omega_{RF} \xi) + \omega_{RF} \sin(\omega_{RF} \xi) + \\
 &\quad - in\omega_R \exp(-in\omega_R t) \cos(-\omega_{RF} t + \omega_{RF} \xi) - \omega_{RF} \exp(-in\omega_R t) \sin \omega_{RF} (\xi - t)]
 \end{aligned}
 \tag{64}$$

$$\begin{aligned}
 I_D &= \int_0^t e^{-in\omega_R t'} \sin \omega_{RF} (t' - \xi) dt' = \frac{1}{(n^2 \omega_R^2 - \omega_{RF}^2)} [in\omega_R \sin(\omega_{RF} \xi) - \omega_{RF} \cos(\omega_{RF} \xi) + \\
 &\quad - in\omega_R \exp(-in\omega_R t) \sin \omega_{RF} (\xi - t) + \omega_{RF} \exp(-in\omega_R t) \cos \omega_{RF} (\xi - t)]
 \end{aligned}
 \tag{65}$$

with

$$2\omega_{RF} \alpha = \frac{\pi}{2}, \tag{66}$$

and

$$\xi = 2\tau - \alpha. \tag{41}$$

For Dipolar Coupling (D)—

$$\begin{aligned}
F_{1(D)} = & \bar{H}_D^0 = \omega_D I_z I_z \\
& - \omega_D I.I \\
& + \frac{1}{4\tau} \frac{\omega_D}{\omega_{RF}} I_x I_x [2\omega_{RF} (2\tau \\
& + \alpha)] \\
& + \sin 2\omega_{RF} (2\tau \\
& - \alpha)] \\
& + \frac{1}{4\tau} \frac{\omega_D}{\omega_{RF}} I_y I_y [2\omega_{RF} (2\tau - \alpha)] - \sin 2\omega_{RF} (2\tau - \alpha)] \\
& - \frac{1}{2\tau} \frac{\omega_D}{\omega_{RF}} [I_x I_y \\
& + I_y I_x] \sin^2 \omega_{RF} (2\tau - \alpha)
\end{aligned} \tag{67}$$

$$\begin{aligned}
\Lambda_{1(D)}(t) = & \sum_{n=-2}^{+2} C_n^{ij} \left[3(I_E I_{iz} I_{jz} + I_F I_{ix} I_{jx}) - \frac{3}{2} I_I (I_{ix} I_{jz} + I_{iz} I_{jx}) + \left(\frac{1}{in \omega_R} \right) (e^{-in \omega_R t} - 1) I.I \right. \\
& + 3(I_E I_{ix} I_{jx} + I_F I_{iy} I_{jy}) - \frac{3}{2} I_I (I_{ix} I_{jy} + I_{iy} I_{jx}) + \frac{1}{in \omega_R} (e^{-in \omega_R t} - 1) I.I + 3(I_H I_{ix} I_{jx} + I_G I_{iy} I_{jy}) \\
& \frac{3}{2} I_J (I_{ix} I_{jy} + I_{jy} I_{jx}) + \frac{1}{in \omega_R} (e^{-in \omega_R t} - 1) I.I + 3(I_E I_{iz} I_{jz} + I_F I_{ix} I_{jx}) + \frac{3}{2} I_I (I_{ix} I_{jz} + I_{iz} I_{jx}) \\
& \left. + \frac{1}{in \omega_R} (e^{-in \omega_R t} - 1) I.I - \frac{1}{in \omega_R} (e^{-im \omega_R t} - 1) (3I_{iz} I_{jz} - I.I) - t F_{1(D)} \right]
\end{aligned} \tag{68}$$

where I_E , I_F , I_G , I_H , I_I and I_J are given by:

$$\begin{aligned}
I_E = & \int_0^t e^{-in \omega_R t'} \cos^2(\omega_{RF} t') dt' = \frac{1}{2n} \frac{\omega_R}{(n^2 \omega_R^2 - 4\omega_{RF}^2)} \left[-2in^2 \omega_R^2 + 4i \omega_{RF}^2 + i \exp(-in \omega_R t) n^2 \omega_R^2 \right. \\
& \left. + in^2 \omega_R^2 \exp(-in \omega_R t) \cos(2\omega_{RF} t) - 2\omega_{RF} \exp(-in \omega_R t) \sin(2\omega_{RF} t) n \omega_R - 4i \exp(-in \omega_R t) \omega_{RF}^2 \right]
\end{aligned} \tag{69}$$

$$\begin{aligned}
I_F = \int_0^t e^{-in\omega_R t'} \sin^2(\omega_{RF} t') dt' = & -\frac{1}{2} \frac{\omega_R}{n(n^2\omega_R^2 - 4\omega_{RF}^2)} \left[-4i\omega_{RF}^2 - i \exp(-in\omega_R t) n^2\omega_R^2 \right. \\
& \left. + in^2\omega_R^2 \exp(-in\omega_R t) \cos(2\omega_{RF} t) - 2\omega_{RF} \exp(-in\omega_R t) \sin(2\omega_{RF} t) n\omega_R - 4i \exp(-in\omega_R t) \omega_{RF}^2 \right]
\end{aligned}
\tag{70}$$

$$\begin{aligned}
I_G = \int_0^t e^{-in\omega_R t'} \sin^2 \omega_{RF} (t' - \xi) dt' = & -\frac{1}{2} \frac{\omega_R}{n(n^2\omega_R^2 - 4\omega_{RF}^2)} \left[2in^2\omega_R^2 - 4i\omega_{RF}^2 - 2in^2\omega_R^2 \cos^2(\omega_R \xi) - in^2\omega_R^2 \exp(-in\omega_R t) \right. \\
& \left. + n^2\omega_R^2 \exp(-in\omega_R t) \cos 2\omega_{RF}(\xi - t) + \right. \\
& \left. + 2\omega_{RF} \exp(-in\omega_R t) \sin 2\omega_{RF}(\xi - t) n\omega_R + 4i \exp(-in\omega_R t) \omega_{RF}^2 \right]
\end{aligned}
\tag{71}$$

$$\begin{aligned}
I_H = \int_0^t e^{-in\omega_R t'} \cos^2 \omega_{RF} (t' - \xi) dt' = & \frac{1}{2} \frac{\omega_R}{n(n^2\omega_R^2 - 4\omega_{RF}^2)} \left[-2in^2\omega_R^2 \cos^2(\omega_R \xi) + 4i\omega_{RF}^2 \right. \\
& \left. + in^2\omega_R^2 \exp(-in\omega_R t) - 4\omega_{RF} n\omega_R \sin(\omega_{RF} \xi) \cos(\omega_{RF} \xi) - 4i \exp(-in\omega_R t) \omega_{RF}^2 \right. \\
& \left. + in^2\omega_R^2 \exp(-in\omega_R t) \cos 2\omega_{RF}(\xi - t) + 2\omega_{RF} \exp(-in\omega_R t) \sin 2\omega_{RF}(\xi - t) n\omega_R \right]
\end{aligned}
\tag{72}$$

$$\begin{aligned}
I_I = \int_0^t e^{-in\omega_R t'} \sin(2\omega_{RF} t') dt' \\
= \frac{1}{(n^2\omega_R^2 - 4\omega_{RF}^2)} [-2\omega_{RF} + 2\omega_{RF} \exp(-in\omega_R t) \cos(2\omega_{RF} t) + in\omega_R \exp(-in\omega_R t) \sin(2\omega_{RF} t)]
\end{aligned}
\tag{73}$$

$$I_J = \int_0^t e^{-in\omega_R t'} \sin 2\omega_{RF} (t' - \xi) dt' = \frac{-1}{(n^2\omega_R^2 - 4\omega_{RF}^2)} \left[-2\omega_{RF} + 4\omega_{RF} \cos^2(\omega_{RF}\xi) + \right. \\ \left. - 2in\omega_R \sin(\omega_{RF}\xi) \cos(\omega_{RF}\xi) - 2\omega_{RF} \exp(-in\omega_R t) \cos 2\omega_{RF}(\xi - t) + \right. \\ \left. + in\omega_R \exp(-in\omega_R t) \sin 2\omega_{RF}(\xi - t) \right] \quad (74)$$

For Quadrupolar interaction (Q)—Using Fig. 3 for the magic echo pulse sequence, we have the first order term of the FME

$$F_{1(Q)} = \bar{H}_{\omega_Q}^0 = \frac{1}{7\tau} \frac{12\alpha\omega_Q}{\pi} I_{x,2} + \frac{4(3\alpha - \tau)\omega_Q}{7\tau} [I_{x,1}I_{x,1} + I_{y,1}I_{y,1} - 2I_{z,1}I_{z,1}] \quad (75)$$

The free evolution diagram in this case is given by the following figure

In this scheme, we have the following relation for each part

$$a_k^{(1)} = \frac{1}{\tau_R} \int_0^{\tau-2\alpha} e^{ik\omega_R t'} dt' \quad (76)$$

$$a_0^{(1)} = \frac{1}{\tau_R} (\tau - 2\alpha) \quad (77)$$

$$a_k^{(1)} = \frac{1}{ik2\pi} \left[e^{ik\omega_R(\tau-2\alpha)} - 1 \right] \quad (78)$$

$$a_k^{(2)} = \frac{1}{\tau_R} \left[\int_{\tau}^{2\tau-\alpha} e^{ik\omega_R t'} dt' + \int_{6\tau+\alpha}^{7\tau} e^{ik\omega_R t'} dt' \right] \quad (79)$$

$$a_0^{(2)} = \frac{1}{\tau_R} (2\tau - 2\alpha) \quad (80)$$

$$a_k^{(2)} = \frac{1}{ik2\pi} \left[e^{ik\omega_R(2\tau-\alpha)} - e^{ik\omega_R\tau} + e^{ik\omega_R 7\tau} - e^{ik\omega_R(6\tau+\alpha)} \right] \quad (81)$$

However, for mathematical convenience, we made the following approximation: we neglected the first free evolution time, and considered the free evolution time given in the following figure:

In this new dynamics picture, the toggling frame is written as

$$\tilde{H}_{(Q)}(t) = \tilde{H}_{(2)} + \tilde{H}_{(3)}\theta(t) + \tilde{H}_{(4)} + \tilde{H}_{(5)} + \tilde{H}_{(6)} + \tilde{H}_{(7)} + \tilde{H}_{(8)}(1 - \theta(t)), \quad (82)$$

Where the terms $\tilde{H}_{(2)}$, $\tilde{H}_{(3)}$, $\tilde{H}_{(4)}$, $\tilde{H}_{(5)}$, $\tilde{H}_{(6)}$, $\tilde{H}_{(7)}$, and $\tilde{H}_{(8)}$ correspond to the toggling Hamiltonian during the intervals δ_2 , δ_3 , δ_4 , δ_5 , δ_6 , δ_7 , δ_8 , respectively, as it is given in the article¹¹. Processing as shown previously, the first and second part of the sequence can be written respectively as

$$a_k^{(1)} = \frac{1}{\tau_R} \int_0^{\tau+2\alpha} e^{ik\omega_R t} dt \quad (83)$$

$$a_k^{(2)} = \frac{1}{\tau_R} \int_{5\tau+3\alpha}^{6\tau+2\alpha} e^{ik\omega_R t} dt. \quad (84)$$

From the above equations, we obtain the following criteria

$$a_0 = c - \phi \quad (85)$$

and

$$a_k = a_k^{(2)} = a_k^{(1)} e^{ik2\pi(5c+\phi)} = \frac{1}{2\pi ik} \left[e^{ik2\pi(c+\phi)} - e^{ik4\pi\phi} \right] e^{ik2\pi(5c+\phi)} \quad (86)$$

where

$$\phi = \frac{\alpha}{\tau_R} \quad (87)$$

and

$$\tau = c\tau_R. \quad (88)$$

The first order FME is computed to be:

$$\begin{aligned}
\Lambda_{1(Q)}(t) &= \sum_{n=-2}^{+2} C_n^{(Q)} \left[12 (I_E I_{z,1} I_{z,1} + I_F I_{y,1} I_{y,1}) + 6 I_{z,2} I_I - 5 \left(\frac{1}{i n \omega_R} \right) (e^{-i n \omega_R t} - 1) I \cdot I + 12 I_E I_{y,1} I_{y,1} + 12 I_F I_{x,1} I_{x,1} - 6 I_I I_{z,2} \right] \\
&\quad (89)
\end{aligned}$$

Considering Fig. 6, we remark that the magic echo pulse sequence removes the $\theta(t)$ dependence and calculation of F_1 and $\Lambda_1(t)$ become less lengthy.

V. Discussion

The zero-order term of the AHT was calculated for the chemical shift, dipolar, and quadrupolar interactions when irradiated with the magic-echo pulse sequence. The results of the AHT (Eqs. (35)-(37)) were shown for a static case where the AHT is more appropriated and sufficient for studying the dynamics of the spin system subject to RF perturbations. In contrast to magic-angle spinning (MAS) where the anisotropic part of the interaction vanishes for any crystallite orientation, pulses disturb the initial state of equilibrium and initiate the evolution of the density operator⁴¹. For long sequences, to avoid complex calculations, the evolution in the presence of an average Hamiltonian is considered. In this approach, a time-dependent Hamiltonian of the system over one cycle is replaced by an equivalent time-independent average Hamiltonian. The time evolution of the system from the initial state ($\rho(0)$), to the state at time $t = t_C$ is given by the solution of the Liouville-von-Neumann equation, $\rho(t_C) = U_{RF} U_{int} \rho(0) U_{int}^{-1} U_{RF}^{-1}$, where U_{int} is given by the Magnus expansion^{3,4}. The propagator U_{RF} represents the interaction associated with the sequence of RF pulses applied over a cyclic time (t_C) and accounts for the rotations imparted to the system. The propagator U_{RF} is given by the Dyson series. The density operator $\rho(t_C)$ can thus be derived from $\rho(0)$ by successive applications of time-evolution operators $U_{RF} U_{int}$ corresponding to the various periods of the pulse sequence.

The similarity between the calculated zero-order term of the average Hamiltonian (Eqs. (35)-(37)) of the three interactions studied in this paper stem from the presence of the

factors $\frac{\Delta\omega}{\tau\omega_{RF}}$, $\frac{\omega_D}{\tau\omega_{RF}}$, and $\frac{\omega_Q}{\tau\omega_{RF}}$ (note that, $2\omega_{RF}\alpha = \frac{\pi}{2}$), for the chemical shift anisotropy, dipolar, and quadrupolar interaction, respectively. This tell us that, the strength of the resonance offset, dipolar, and quadrupolar coupling constants is an important factor to consider when using the theory of average Hamiltonian to control the spin dynamics, in particular when dealing with the convergence of the Magnus expansion. Furthermore, looking to the Eqs. (35)-(37), it can be seen that the dynamics are more complex for Eq. (37) due to the N-dimensional Hilbert space arising from the quadrupolar spin nuclei. Therefore, for numerical computations, efficient truncation of the Magnus expansion will be expected for quadrupolar spins. With stronger RF power for example, the first order terms of the Magnus expansion for the three interactions studied (CSA, dipolar, and quadrupolar) can be

further reduced. The AHT is valid only for full rotor periods and thus cannot describe essential aspects of the experiments at all times such as the appearance of sidebands.

For the Fer expansion, it can be seen from Eqs. (18)-(22) that, the calculation of the obtained results in the Eqs. (38)-(40), involves a serie of nested commutators resulting in the Eq. (22). The results of F_1 obtained for chemical shift, dipolar, and quadrupolar interactions (Eqs. (38)-(40)) might lead to the average Hamiltonian, $\overline{H}$, in the sense of Magnus expansion under the following circumstances:

$$\frac{F_1(\tau_C)}{\tau_C} = \overline{H} \quad (90-a)$$

where τ_C is the cyclic time (period of H). The difference between Magnus and Fer expansions lies in the form of the correction terms. The result of the Eq. (19) and the knowledge of the Hamiltonian $H(t)$ in the Fer approach leads to a straightforward calculation of the Eq. (42). $H_F^{(1)}$ is the time integral function which is used in the calculation of F_2 . The iteration process can continue easily when the initial values of $F_n(t)$ and $H_F^{(n)}$ are found. One major advantage of the Fer expansion over the AHT (Magnus expansion) is that only an evaluation of nested commutators is required in the calculation of $H_F^{(n)}$ (Eq. (22)). The Magnus expansion requires the calculation of nested commutators and their integrals to obtain the correction terms of a Hamiltonian (Eqs. (5), (6), etc). Blanes and al²⁷ had proofed the convergence of the Fer expansion and shown that the convergence of Fer expansion is much faster than that of Magnus expansion. Madhu and Kurar²⁴ also highlighted the observations such that the calculation of a term like $H_F^{(1)}$ will contain several of the important signatures of the various higher-order terms in Magnus expansion where all of which need to be calculated independently. In addition, they mentioned that, the calculation of the infinite number of commutators in Eq. (22), although looking imposing, may turn out to be simpler to handle in most experimentally interesting cases due to the fast convergence and the negligible value of many of the commutators. Both approaches (Fer and AHT) may be complimentary and provide solutions to the time-dependent Schrodinger equation:

$$\frac{dU}{dt} = -iH(t)U(t). \quad (90-b)$$

In the general case, there is no compact formula for the solution of the above equation, unless H is time independent or H commutes with itself at two different times^{42,43}. The Fer and Magnus proposals endeavor to complement the general solution

$$U(t) = \exp\left(\int_0^t dt' H(t')\right) U_0 \quad (90-c)$$

in two different directions. A salient feature of the Fer and Magnus expansions stem from the fact that, when $H(t)$ is an element in a given Lie algebra group, both approaches have the required structure and evolve in the desired group (Lie group). Furthermore, this is also true for their truncation to any order.

Next, In part IV. 3, when using the Floquet-Magnus expansion, we considered a sample-spinning experiment. Indeed, the concept of AHT was found to be less descriptive for rotating systems, and these types of experiments were found to be more conveniently described using Floquet theory^{2,7,8}. As mentioned in the introduction part, the Floquet theory has not been studied in this article, but instead we used the Floquet-Magnus expansion that shed light on AHT and FLT. Like the FLT, FME describes the time evolution of the spin system at all times. As can be seen in this section, (part IV. 3), the FME is more useful in simplifying calculations and providing a more intuitive understanding of spin dynamics processes. In the article by Mananga and Charpentier² (Eq. 54), we shown that the lowest-order term F_1 as provided by AHT, FLT, and FME are all identical. The lowest-order term in the current paper is reported to: Eq. (35) = Eq. (60); Eq. (36) = Eq. (67); Eq. (37) = Eq. (75). Next, using the FME, we calculated for each interaction, the first order function ($\Lambda_1(t)$) that provides an easy way for evaluating the spin system evolution. This function $\Lambda_1(t)$ is connected to the appearance of features like spinning sidebands in MAS. The evaluation of $\Lambda_1(t)$ is useful especially for the analysis of the non-stroboscopic evolution. In the article by Mananga and al²², it is shown that the second order ($\Lambda_2(t)$) is small in comparison to the first order ($\Lambda_1(t)$), and will be less useful in many cases. The function $\Lambda_1(t)$, available only in the FME scheme, will be useful to describe the spin dynamics in solid-state NMR and understanding different synchronized or non-synchronized experiments.

VI. Conclusion

The FME and the FE are two emerging approach in solid state NMR that deserve further attention. Both theories still need more quantitative work to expand their use in the field of solid-state NMR. In the articles^{22,23}, we studied spin dynamics under dipolar interactions using the FME. However, in this paper, we present the application of the AHT and FME approaches to the most useful interactions (CS, D, Q) in solid-state NMR. We also attempted to adapt the use of Fer expansion to these various forms of NMR interactions. Because of the symmetry of the magic echo pulse sequence, the calculation of the $\Lambda_1(t)$ function tend to be less lengthy and probably of significant use. We hope that this paper will help appreciate the application of some emerging theories in solid-state NMR such as the Floquet-Magnus expansion and the Fer expansion to the investigation of NMR interactions. Note that the FME is an extension of the popular Magnus Expansion and Average Hamiltonian Theory. It aims is to bridge the AHT to the Floquet Theorem but in a more concise and efficient formalism. Calculations can then be performed in a finite-dimensional Hilbert space instead of an infinite dimensional space within the so-called Floquet theory. We expected that the FME will provide means for more accurate and efficient Spin dynamics simulation and for devising new RF pulse sequence.

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Appendix

A1. The spin-1 operator formalism of Vega and Pines is given by the following spin operators³³:

$$I_{p,1} = \frac{1}{2} I_p \quad (91)$$

$$I_{p,2} = \frac{1}{2} (I_p I_r + I_r I_q) \quad (92)$$

$$I_{p,3} = \frac{1}{2} (I_r^2 - I_q^2) \quad (93)$$

with $p = x, y, z$ and $(p, q, r) = (x, y, z)$ with cyclic permutation.

A2. Calculation of $\Lambda_{1(CSA)}(t)$

$$\tilde{H}_{CSA}(t) = \tilde{H}_{(1)}\theta(t) + \tilde{H}_{(2)} + \tilde{H}_{(3)} + \tilde{H}_{(4)} + \tilde{H}_{(5)} + \tilde{H}_{(6)}(1 - \theta(t)) \quad (94)$$

$$\begin{aligned}
\Lambda_{1(CSA)}(t) &= \int_0^t \left(\sum_i \omega_{CS,0}^i(t') \right) I_{iz} \left(\sum_{k=-\infty}^{+\infty} a_k e^{-ik\omega_R t'} \right) dt' \\
&+ \int_0^t \left(\sum_i \omega_{CS,0}^i(t') \right) \left(I_z^i \cos(\omega_{RF} t') \right. \\
&\quad \left. - I_x^i \sin(\omega_{RF} t') \right) dt' \\
&+ \int_0^t \left(\sum_i \omega_{CS,0}^i(t') \right) \left(\right. \\
&\quad \left. - I_x^i \cos(\omega_{RF} t') \right. \\
&\quad \left. + I_y^i \sin(\omega_{RF} t') \right) dt' + \int_0^t \left(\sum_i \omega_{CS,0}^i(t') \right) \left(\right. \\
&\quad \left. - I_x^i \cos \omega_{RF} t' \right. \\
&\quad \left. - \xi + I_y^i \sin \omega_{RF} t' \right. \\
&\quad \left. - \xi \right) dt' \\
&+ \int_0^t \left(\sum_i \omega_{CS,0}^i(t') \right) \left(\right. \\
&\quad \left. - I_z^i \cos(\omega_{RF} t') \right. \\
&\quad \left. - I_x^i \sin(\omega_{RF} t') \right) dt' \\
&+ \int_0^t \left(\sum_i \omega_{CS,0}^i(t') \right) I_z^i \left(\sum_{k=-\infty}^{+\infty} a_k e^{-ik\omega_R t'} \right) dt' \\
&+ \int_0^t \left(\sum_i \omega_{CS,0}^i(t') \right) I_z^i dt' - tF_1
\end{aligned} \tag{95}$$

A3. Calculation of $\Lambda_{1(Q)}(t)$

$$\begin{aligned}
\Lambda_{1(Q)}(t) &= \int_0^t \tilde{H}_2 dt + \int_0^t \tilde{H}_3 \theta(t') dt' + \int_0^t \tilde{H}_4 dt' + \int_0^t \tilde{H}_5 dt' + \int_0^t \tilde{H}_6 dt' + \int_0^t \tilde{H}_7 dt' + \int_0^t \tilde{H}_8 (1 - \theta(t')) dt' - tF_1
\end{aligned} \tag{96}$$

We have considered the first-order quadrupolar coupling and neglected all the secular components for the second-order quadrupolar coupling. We have

$$H_Q = \sum_i \omega_{Q,0}^i(t) \frac{1}{\sqrt{6}} (3I_{iz}^2 - I_i^2). \tag{29}$$

$$\omega_{Q,0}(t) = \sum_{m=-2}^{+2} \omega_{Q,0}^{(m)} e^{im\omega_R t}, \quad (97)$$

$\omega_{Q,0}^{(m)}$ is a constant. Let us write the following

$$\omega_{Q,0}(t) = \sum_{n=-2}^{+2} C_n^{(Q,m')}(\alpha, \beta, \gamma) e^{-in\omega_R t} = \sum_{n=-2}^{+2} \omega_{Q,m'}^{(n)} e^{-in\omega_R t} \quad (98)$$

$$\begin{aligned} \Lambda_{1(Q)}(t) = & \int_0^t \left(\sum_i \omega_{Q,0}^i(t') \right) \left[12I_{z,1}I_{z,1} \cos^2(\omega_{RF}t') + 12I_{y,1}I_{y,1} \sin^2(\omega_{RF}t') + 6I_{z,2} \sin(2\omega_{RF}t') - II \right] dt' \\ & \int_0^t \left(\sum_i \omega_{Q,0}^i(t') \right) \left[12I_{y,1}I_{y,1} - II \right] \left(\sum_{k=-\infty}^{+\infty} a_k e^{-ik\omega_R t'} \right) dt' + \int_0^t \left(\sum_i \omega_{Q,0}^i(t') \right) \left[12I_{y,1}I_{y,1} \cos^2(\omega_{RF}t') \right] dt' \\ & \int_0^t \left(\sum_i \omega_{Q,0}^i(t') \right) \left[12I_{x,1}I_{x,1} \sin^2(\omega_{RF}t') - 6I_{z,2} \sin(2\omega_{RF}t') - II \right] dt' + \int_0^t \left(\sum_i \omega_{Q,0}^i(t') \right) \left(12I_{x,1}I_{x,1} \cos^2(\omega_{RF}t') \right) dt' \\ & \int_0^t \left(\sum_i \omega_{Q,0}^i(t') \right) \left[12I_{z,1}I_{z,1} \sin^2(\omega_{RF}t') + 6I_{y,2} \sin(2\omega_{RF}t') - II \right] dt' + \\ & + \int_0^t \left(\sum_i \omega_{Q,0}^i(t') \right) \left[12I_{x,1}I_{x,1} \cos^2(\omega_{RF}(t' - \xi)) \right] dt' \\ & \int_0^t \left(\sum_i \omega_{Q,0}^i(t') \right) \left[12I_{z,1}I_{z,1} \sin^2(\omega_{RF}(t' - \xi)) - 6I_{y,2} \sin(2\omega_{RF}(t' - \xi)) - II \right] dt' \\ & + \int_0^t \left(\sum_i \omega_{Q,0}^i(t') \right) \left[12I_{y,1}I_{y,1} - II \right] \left[1 - \sum_{k=-\infty}^{+\infty} a_k e^{-ik\omega_R t'} \right] dt' \\ & + \int_0^t \left(\sum_i \omega_{Q,0}^i(t') \right) \left[12I_{x,1}I_{x,1} \cos^2(\omega_{RF}t') + 12I_{y,1}I_{y,1} \sin^2(\omega_{RF}t') + 6I_{z,2} \sin(2\omega_{RF}t') - II \right] dt' - tF_1 \end{aligned} \quad (99)$$

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Fig. 1. Magic echo sequence for the time-reversing the evolution of a system of nuclear-spins coupled by a dipolar interaction.

Fig. 2.
Simple two pulse quadrupolar echo sequence.

Fig. 3.
Magic echo sequence for refocusing the quadrupolar interaction.

Fig. 4.

Free evolution times in the magic echo sequence. The relation $\theta_2(t) = 1 - \theta_1(t)$ is only valid during the interval of free evolution time i.e, where $\theta(t)$ acts.

Fig. 5.

The relation $1-\theta(t)$ is only valid during the interval where $\theta(t)$ acts.

Fig. 6. Magic echo sequence for refocusing the quadrupolar interaction with the first free evolution time shown in Fig.3, neglected.

Table 1

useful theories in solid-state NMR

Theory	Application	Acronym	Publication date	References
Floquet-Magnus Expansion	Spin dynamics in solid-state NMR, synchronized and non-synchronized experiments	FME	2011	J. Chem. Phys. 135, 044109 (2011)
Fer Expansion	Alternative approach to solve time-dependent linear differential equations	FE	2006	Chem. Phys. Lett. 418, 235 (2006); Bull. Classe Sci. Acad. R. Belg. 44, 818 (1958)
Floquet Theory	Dynamics of spin system at all times, multiple incommensurate frequencies	FLT	1982	Phys. Rev. B, 25, 6622 (1982); J. Chem. Phys., 79, 548 (1983); Ann. Econ. Norm. Suppl. 12, 47 (1883)
Average Hamiltonian Theory Magnus Expansion ³	Stroboscopic and synchronized manipulations	AHT	1968	Phys. Rev. 175, 453 (1968) Comm. Pure Appl. 7, 649 (1954)
Static Perturbation Theory	Systems with a finite number of levels	SPT	1982	J. Chem. Phys. 77, 4360 (1982)
Secular Averaging Theory	Sample rotation and pulse crafting	SAT	1976	Principles of high resolution NMR in solids, 2 nd Ed. (Springer, Berlin, 1976).
Dison Series	Quantum mechanics and dynamics, scattering theory		1949	Phys. Rev. 75, 1736 (1949)
Wilcox Expansion	Elementary parameter-differentiation techniques		1967	J. Math. Phys. 8, 962 (1967)
Van Vleck Transformation	Highly degenerate systems, e.g., dipolar broadened	VVT	1929	Phys. Rev. 33, 467 (1929)