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Progress in Spin Dynamics Solid-State Nuclear Magnetic Resonance with the Application of Floquet-Magnus Expansion to Chemical Shift Anisotropy

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Abstract

The purpose of this article is to present an historical overview of theoretical approaches used for describing spin dynamics under static or rotating experiments in solid state nuclear magnetic resonance. The article gives a brief historical overview for major theories in nuclear magnetic resonance and the promising theories. We present the first application of Floquet-Magnus expansion to chemical shift anisotropy when irradiated by BABA pulse sequence.

Keywords

Solid-State NMR; Average Hamiltonian Theory; Floquet Theory; Floquet-Magnus Expansion; BABA Pulse sequence; CSA

I. Introduction

Soon after finishing his graduate studies, Erwin Hahn burst on the world of science with his remarkable observation of spin echoes. This discovery provided key impetus to the development of pulse methods in nuclear magnetic resonance (NMR), and must therefore be ranked among the most significant contributions to magnetic resonance¹. Since the discovery of spin echoes in 1950 by Hahn², all manipulations of spins and spin interaction by radio-frequency or microwave pulses have been accurately described by quantum mechanics and mathematics that lend to creativity and new insights. Nowadays, the technique of NMR is a vibrant and central area of research, with contributions from scientists in nearly all fields of physical, chemical, biological sciences, and mathematics. Though there are multiple levels of complexity, the technique of magnetic resonance has been made simple to the end user: a sample of interest is placed in a strong magnetic field, followed by the application of radio-frequency or microwave pulses, and the resulting signal emitted by the sample is detected^{3–5}.

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Various theories have been developed and introduced over time in magnetic resonance to predict, describe or control coherently the dynamics governing spin systems. These theories include but are not limited to Floquet theory (FLT) ^{6,7}, average Hamiltonian theory (AHT) ^{8,9}, Floquet-Magnus expansion (FME) ^{6,8,10}, and Fer expansion (FE) ^{11,12}. The paper is organized as follows: the next section summarizes the essential background information about the FLT, AHT, FME, and FE. The first application of the FME to the chemical shift anisotropy (CSA) when irradiated with the BABA pulse sequence is presented in the sub-section II.4. Finally, section III of the paper discuss and summarizes our conclusions.

II. Various Theories in Solid-State Nuclear Magnetic Resonance

Numerous approaches have been used in solid-state NMR. Out of these approaches, only AHT and FLT have been widely utilized, whereas the Fer and Floquet-Magnus expansions were introduced very recently to NMR. The AHT is a perturbative approach while the FLT is a more general approach than AHT. The Floquet theory approach has been a powerful method for describing the full time dependence of the response of a periodically time-dependent system. The FLT method provides a framework for treating time-dependent Hamiltonians in NMR in a way that can easily be extended to several non-synchronized modulations ¹³⁻¹⁶. For instance, it can be applied to time-dependent quantum systems exploiting the propagator for a periodic Hamiltonian that lead to a time-independent Hamiltonian. Under such circumstances of the time-independent Floquet Hamiltonian approach, the time-dependent Hilbert-space Hamiltonian is transformed into an infinite-dimensional Hilbert space ^{7,17,18}. For numerical computations, the infinite dimension of the Hilbert space has to be truncated. Matrix representations are usually used when the FLT is applied to spectroscopy ^{13,20,22}. The value and applicability of this approach lead Shirley ⁷ in 1965 to introduce this scheme to spectroscopy to solve the periodically time-dependent Schrodinger equation. From this initial introduction of FLT to quantum physics, the field of nuclear magnetic resonance spectroscopy has gained momentum with a continuous stream of conceptual advances and methodological innovations with new applications continuously increasing ¹⁹⁻²⁴. The two milestones theoretical approaches (AHT, FLT) and the two newly introduced theoretical approaches (FE, FME) used for NMR include:

II.1. Average Hamiltonian Theory

The AHT was developed by John Waugh and co-workers in 1968 ⁹ to study the dynamics of a spin system subject to an RF perturbation. The AHT approach is the most common used method to treat theoretical problems in solid-state NMR and have been used sometimes abusively. This approach explains the average motion of the spin system, the effects of multiple-pulse sequences, and the effects of a time-dependent perturbation applied to the system. The basic understanding of AHT consists to consider a time dependent Hamiltonian $H(t)$ governing the spin system evolution, and describe the effective evolution by an average Hamiltonian $\bar{H}$ within a periodic time (T). This is satisfied only if $H(t)$ is periodic(T) and the observation is stroboscopic and synchronized with period (T). Two major expansions (Baker-Cambell-Hausdorff and Magnus) and an exact computation including the diagonalization of the time evolution operator defined the average Hamiltonian ⁶². The main result of AHT is given by

$$\bar{H}_0 = \bar{H}_0^{(0)} + \bar{H}_0^1 + \bar{H}_0^2 + \dots \quad (1)$$

with

$$\overline{H}_0^{(0)} = \frac{1}{t_c} \int_0^{t_c} dt_1 \tilde{H}_0(t_1), \quad (2)$$

$$\overline{H}_0^{(1)} = \frac{-i}{2t_c} \int_0^{t_c} dt_2 \int_0^{t_2} dt_1 [\tilde{H}_0(t_2), \tilde{H}_0(t_1)], \quad (3)$$

...

...

where $\tilde{H}_0(t)$ is the toggling frame Hamiltonian. The toggling frame Hamiltonian is the Hamiltonian in the time-dependent interaction representation with respect to the perturbed Hamiltonian. The central result of AHT (Eq. (1)) is obtained by expressing the evolution propagator $U(t_c)$ (given in section III) by an average Hamiltonian $\overline{H}_0$ and using the Magnus expansion⁶² which forms the basis of AHT.

The AHT technique has been widely used in the NMR literature in the development of multiple pulse sequences^{25,26,29} and in the context of both decoupling and recoupling experiments^{20,22}. The AHT set the stage for stroboscopic manipulations of spins and spin interactions by radio-frequency pulses and also explains how periodic pulses can be used to transform the symmetry of selected interactions in coupled, many-spin systems considering the average or effective Hamiltonian of the RF pulse train²⁵. Though holding well for static experiments, the AHT suffers from the following shortcomings. (a) This technique does not sufficiently describe the case of magic angle spinning (MAS) spectra^{20,27,28}. In the case of MAS, the signal is usually observed continuously with a time resolution much shorter than the rotor period. (b) One has to be able to define a single basic frequency as well as a cycle time of the Hamiltonian. (c) The AHT cannot be used with multiple incommensurate time-dependent processes in solid-state NMR such as sample rotation and non-synchronized radio frequency irradiation^{10,20,22}. The convergence of the series expansion of the Hamiltonian can be a problem and the basic frequency has to be larger than the transition frequencies in the Hamiltonian. Recently, the validity of the AHT method was probed for quadrupolar nuclei²¹. The investigation showed that the AHT method becomes less efficient to predict the dynamics of the spin system as the quadrupolar spin nuclei dimension increase. This is attributed to the Hilbert space becoming very large and leading to the contribution of non-negligible higher order terms in the Magnus expansion being truncated. For instance, considering a simple two-pulse sequence for refocusing the quadrupolar Hamiltonian shown in Fig. 1, Mananga et al.²¹ have shown that the ability of the AHT to predict the spin dynamics depends on the size of the spin system. Figs. 2, 3, and 4 obtained numerically for spin $I=1$, $3/2$, and $5/2$ show how close the AHT approach can be to the exact numerical result from the Liouville Von Neumann (VN) equation for each type of spin systems²¹. These figures show that the first-order AHT predicts the spin dynamics for spin $I=1$ over a large bandwidth, and for relatively large pulse spacing compared to spin $I=3/2$ and $5/2$. Figures in this manuscript are reproduced from my earlier published work. Reprinted from Ref.²¹, Copyright (2008), with permission from Elsevier. The vertical axis in Figs. 2, 3, and 4 represents the absolute value of the difference of the observable single quantum coherences of the density matrix. The vertical axis in Fig. 2 scale from 0 to 0.55, in Fig. 3 scale from 0 to 4, and in Fig. 4 scale from 0 to 15. The horizontal axis for all the figures (Figs. 2, 3, and 4) scale from 0 to 250 kHz. This horizontal axis represents the scale of the quadrupolar frequencies (ω_q).

The Liouville-von Neumann equation is the basic frame work in quantum statistic mechanics that provides a unified description of dynamical and statistical phenomena⁶³. The

advantage of this approach is the ability to monitor the dynamics instantaneously, resulting in physical insight. The authors²¹ in figures 2, 3, and 4 used the simple two-pulse cycle to compare the accuracy of the first-order AHT to a numerical solution obtained from the VN equation. The smaller the absolute value of the difference of the single quantum (SQ) coherence between the AHT and the VN solution, the more AHT converges to the exact solution obtained by the VN equation. The figures also show that, as the spin number

increases, $I=1 \rightarrow I=\frac{3}{2} \rightarrow I=\frac{5}{2}$, less AHT predicts the spin dynamics. Furthermore, the agreement for the SQ coherences between AHT and the VN equation is good over a

bandwidth of approximately 50 kHz, when $\tau = 2\mu s$ for both $I=\frac{3}{2}$ and $I=\frac{5}{2}$. But, this agreement was shown to deteriorate for a large pulse spacing of $\tau = 10\mu s$. Figure 2 indicates that the agreement between SQ coherences computed by AHT and the VN equation (spin $I=1$) is relatively independent of the pulse spacing. The AHT failed to converge to a numerical solution obtained by the VN equation. It is expected that as higher order terms of the Magnus expansion are taken into account in the system dynamics, AHT is expected to converge to the solution obtained by the Louville Von Neumann equation. Furthermore, the results indicate that the dynamics appear more complex for the higher spin systems for the range of τ and quadrupolar frequencies (ω_q) studied. This work²¹ focused on a solid-echo pulse sequence, and the efficiency of AHT is intimately tied to this cycle.

II.2. The Floquet Theory

The FLT introduced to the NMR community in the early 1980's simultaneously by Vega^{33,34} and Maricq³² is another illuminating and powerful approach that offers a way to describe the time evolution of the spin system at all times and is able to handle multiple incommensurate frequencies. Floquet theory is an exact method and does not imply any assumptions or approximations. This theory provides a more general approach to AHT and is useful in discussing the convergence of the expansion⁶¹. The theory maps the finite-dimensional time-dependent Hilbert space onto an infinite-dimensional but time-independent Floquet space. Floquet description requires an additional Fourier space to describe the quantization of the motional process. Matrix-based Floquet description leads to a correct description of time-dependent Hamiltonians including the side bands. The FLT 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^{22,23,30,31}. The FLT has been applied satisfactorily to simple-spin systems^{33,34,39}, spin-pair systems⁴⁰⁻⁴² to study important NMR phenomena including rotational-resonance^{30,41,42}, composite pulse sequence designing^{43,44}, field-dependent chemical shifts⁴⁵, cross-polarization dynamics⁴⁶⁻⁴⁸, two-dimensional solution NMR experiments⁴⁹, and the dynamic characteristics of exchanging spin systems^{18,50}. The general description of the FLT is equally applicable to dipolar systems as well as to quadrupolar nuclear spin systems⁵⁸. However, spin system with large quadrupolar couplings may violate the convergence conditions for the expansions employed to evaluate the Floquet matrices³¹. An important question to answer is to know the level of extension the FLT can be used in NMR without losing its conceptual framework. In other words, probing the validity of FLT for quadrupolar nuclei including those with spin $I=1, 3/2, 5/2$, and $7/2$ by analyzing a simple pulse sequence can also be beneficial to the NMR community. While the FLT scheme provides a more universal approach for the description of the full time dependence of the response of a periodically time-dependent system, it is most of the time impractical¹⁰. Analytical calculations are limited to small spin systems and it is difficult to get physical insight from matrix representation. For instance, Matti Maricq³² obtained results that shown that the Floquet theory and the average Hamiltonian theory are equal for each of the first two orders but comparison of higher orders is more difficult.

The full Floquet Hamiltonian has an infinite dimension and it is often not very intuitive to understand its implications on the time evolution of the spin system. Matrices for multimode Floquet calculations can become intractable. Massive reduction in dimensionality by truncation of the Fourier dimensions can introduce artifacts. In the literature, problems with up to three frequencies have been treated, but the demand of experiments that require four frequencies for a full description is increasing^{57,59,60}. For instance, non-cyclic multiple-pulse sequences like two-pulse phase-modulated (TPPM) decoupling experiment³⁷ acquire four frequencies under double rotation (DOR)³⁸ and there are some other obvious problems with four frequencies like triple-resonance CW radio frequency irradiation under MAS³⁰. To the best of my knowledge, the Floquet theory had not been used to analyze solid state NMR Hamiltonian with four or more frequencies.

II.3. The Fer Expansion

The Fer expansion introduced recently to the NMR community by Madhu and Kurur via the use of Bloch-Siegert shift and heteronuclear dipolar decoupling¹². The FE approach is another alternative expansion scheme for solving the time-dependent Schrodinger differential equation formulated by Fer in 1958¹¹. This approach is still in its infancy and can be considered to be complimentary to the Magnus expansion (AHT). The FE requires only an evaluation of nested commutators instead than both an evaluation of nested commutators and their integrals to obtain the correction terms of a Hamiltonian as required the Magnus expansion. While the efficiency of Fer expansion seems obvious, more work is still required to allow the scheme to overcome difficulties such as cases involving non-periodic and non-cyclic cases. Other expansion approaches including Dison series³⁵, Wilcox expansion³⁶, secular averaging theory^{26,51,53,54,55,56}, Van Vleck transformation^{10,22,26,51}, Van Vleck-Primas^{22,26,52} perturbation, static perturbation theory^{10,26} and other emerging theoretical methods deserve further additional attention in the spin physics community.

II.4. The Floquet-Magnus Expansion

Very recently, Mananga and Charpentier introduced the Floquet Magnus expansion¹⁰ approach to solid state NMR and spin physics. The FME scheme is the fusion of the two major methods described above and used to control the spin dynamic systems in solid state NMR, the AHT⁹ and the FLT^{6,7}. The approach of FME makes use of its unique solution that has the required structure and evolves in the desired Lie group. This unique approach in spin physics is useful to shed new lights on AHT and FLT. The FME approach was also compared to the Floquet-Van Vleck approach¹⁰ and the static perturbation theory^{10,26} for simple cases. All three theoretical approaches (AHT, FLT, FME) are equivalent in the first order. This is the popular average Hamiltonian

$$H_{AHT}^{(0)} = H_{eff(FT)}^1 = H_{1(FME)} = H_0. \quad (4)$$

The FME approach can be considered as an improved AHT or a new version of FLT that could be very useful in simplifying calculations and providing a more intuitive understanding of spin dynamics processes. This approach (FME) is essentially distinguished from other theories with its famous function $\Lambda_n(t)$ ($n=1,2,3,\dots$) which provides an easy and alternative way for evaluating the spin behavior in between the stroboscopic observation points^{10,23,24}. In fact, the following equation¹⁰

$$\frac{\Omega(T)}{T} = e^{-i\Lambda(0)} F e^{i\Lambda(0)} \quad (5)$$

is a general approach of the AHT called FME which gives also the option of $\Lambda(0) = 0$. The function $\Lambda_n(t)$ is connected to the appearance of features like spinning sidebands in MAS. The FME general formula are given by¹⁰

$$\Lambda_n(t) = \Lambda_n(0) + \int_0^t G_n(\tau) d\tau - t F_n \quad (6)$$

with

$$F_n = \frac{1}{T} \int_0^T G_n(\tau) d\tau \quad (7)$$

where $n = 1, 2, 3, \dots$

and

$$G_1(\tau) = H(\tau), \quad (8)$$

$$G_2(\tau) = -\frac{i}{2} [H(\tau) + F_1, \Lambda_1(\tau)], \quad (9)$$

$$G_3(\tau) = -\frac{i}{2} [H(\tau) + F_1, \Lambda_2(\tau)] - \frac{i}{2} [F_2, \Lambda_1(\tau)] - \frac{1}{12} [\Lambda_1(\tau), [\Lambda_1(\tau), H(\tau) - F_1]] \quad (10)$$

The $\Lambda_n(t)$ functions ($n = 1, 2, 3, \dots$) represent 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 evaluation of $\Lambda_n(t)$ is useful in many different ways, for instance, in rotating experiment in NMR, this function can be used to quantify the level of productivity of double quantum terms. For example, the function $\Lambda_n(t)$ plotted in Fig. 5 ($n = 1$), was used to investigate the effect of finite pulse errors on BABA pulse sequence²⁴ under dipolar interaction.

However, the choice of the pulse sequences (BABA, C7) used in the papers^{23,24} were not ideal due to lengthy calculations using FME scheme comparatively to the choice of simple examples as multimode Hamiltonian or common form of Hamiltonian in solid-state NMR written in terms of the irreducible tensor operators used in the article¹⁰. Another advantage of the FME approach is that it is not restricted to dipolar or quadrupolar interaction, and can be applied to any case of Hamiltonian such as chemical shift anisotropy (CSA). In our previous work, the FME approach was used to analyze the spin dynamics evolving under the dipolar interaction when irradiated with BABA pulse sequence. This article²³ ignore the effects of chemical shift anisotropy. However, it is important to mention that BABA is not really useful when the CSA are big. On the other hand BABA is useful if the chemical contributions are less important. Therefore, considering the CSA effect is of major importance in studying BABA pulse sequence.

APPLICATION OF THE FME TO THE CSA USING BABA PULSE

Application of the first contribution terms of the Floquet-Magnus expansion to the chemical shift anisotropy when irradiated with the BABA pulse sequence²³ may lead to the condition for the CSA to be averaged out in each rotor period τ_R . The average of the CSA during

sample rotation about a fixed axis and application of a BABA pulse sequence can be evaluated explicitly if we consider the CSA interaction representation Hamiltonian term in the following general form⁶⁴:

$$H_{\text{CSA}}(t) = \sum_i \delta_{\text{CSA}}^i(t) I_z^i \quad (11)$$

where

$$\delta_{\text{CSA}}^i(t) = \sum_{n=-2}^{+2} f_n^i(\alpha, \beta, \sigma^{ii}) \exp \{-in(\omega_r t + \gamma)\} R_{\text{spin}}(t), \quad (ii=XX, YY, ZZ). \quad (12)$$

The coefficients $f_n^i(\alpha, \beta, \sigma^{ii})$ depend on the orientation of the molecule and on the CSA tensor elements. As in Tycko article⁶⁴, let us write the following notation

$$R_{\text{spin}}(t) I_z = I_z \cos \varepsilon + \frac{1}{2} \sin \varepsilon (I_+ e^{-i\zeta} + I_- e^{i\zeta}) \quad (13)$$

where $\varepsilon(t)$ and $\zeta(t)$ specifies the direction of $R_{\text{spin}}(t) I_z$ determined by the BABA pulse sequence. We study the particular case where $\varepsilon(t)$ is small, then $\cos \varepsilon(t) \rightarrow 1$, $\sin \varepsilon(t) \rightarrow 0$, and $R_{\text{spin}}(t) I_z \approx I_z$. For sake of simplicity (but without loss of generality), we rewrite the chemical shift coefficient as following

$$\delta_{\text{CSA}}^i(t) = \sum_{n=-2}^{+2} f_n^i(\alpha, \beta, \sigma^{ii}) \exp \{-in(\omega_r t + \gamma)\}. \quad (14)$$

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

For: $0 \leq t \leq \frac{t_R}{2}$,

$$\tilde{H}_{\text{CSA}}(t) = \sum_i \delta_{\text{CSA}}^i(t) R_X^+ \left(\frac{\pi}{2} \right) I_z^i R_X \left(\frac{\pi}{2} \right) = \sum_i \delta_{\text{CSA}}^i(t) I_y^i = H_Y \quad (15)$$

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

$$\tilde{H}_{\text{CSA}}(t) = \sum_i \delta_{\text{CSA}}^i(t) R_Y^+ \left(\frac{\pi}{2} \right) I_z^i R_Y \left(\frac{\pi}{2} \right) = - \sum_i \delta_{\text{CSA}}^i(t) I_x^i = H_X. \quad (16)$$

Considering the BABA pulse sequence in the same picture as in reference²³,

The toggling frame is written as

$$\tilde{H}_{CSA}(t) = H_Y(t)\theta(t) + H_X(t)(1-\theta(t)) \quad (17)$$

Expanding the time-dependent function $\theta(t)$ in the form of Fourier expansion, we have:

$$\theta(t) = \sum_n a_n e^{-in\omega_R t} \quad (18)$$

where a_n represents the time-dependent Fourier coefficients corresponding to the Fourier index n . These coefficients are derived in the appendix.

The toggling Hamiltonian can be written more explicitly as following

$$\tilde{H}_{CSA}(t) = \sum_i (I_X^i + I_Y^i) \underbrace{\sum_{n=-2}^{+2} f_n^i a_{-n}}_{AHT = \bar{f}_n^{(0)}} + \sum_i (I_X^i + I_Y^i) \sum_{m=-\infty}^{+\infty} e^{-im(\omega_R t + \gamma)} \underbrace{\sum_{n=-2}^{+2} f_n^i a_{m-n}}_{\bar{f}_n^{(m)}} + \frac{1}{2} \sum_i \sum_{n=-2}^{+2} f_n^i(\alpha, \beta, \sigma^i) e^{-in(\omega_R t + \gamma)} (-I_X^i + I_Y^i). \quad (19)$$

The first order average Hamiltonian, which is also the order contribution to the Floquet-Magnus expansion is given by:

$$F_1 = \frac{1}{T} \int_0^T \tilde{H}_{CSA}(t) dt = \frac{1}{\tau_R} \int_0^{\tau_R} \tilde{H}_{CSA}(t) dt = \sum_i \sum_{n=-2}^{+2} f_n^i a_{-n} (I_X^i + I_Y^i) \quad (20)$$

Which lead to the following interesting result

$$F_1 = \sum_i (f_{-1}^i a_1 + f_0^i a_0 + f_1^i a_{-1}) (I_X^i + I_Y^i) \quad (21)$$

or

$$F_1 = \sum_i \left[\frac{1}{\pi i} (f_1^i - f_{-1}^i) + \frac{1}{2} f_0^i \right] (I_X^i + I_Y^i) \quad (22)$$

The criterion for the CSA to be averaged out in each τ_R period is:

$$\frac{1}{\pi i}(f_1^i - f_{-1}^i) + \frac{1}{2}f_0^i = 0. \quad (23)$$

Similar analysis was also applied to dipolar interaction in the article²³. The first order of the argument of the propagator operator in FME approach can be calculated as following:

$$\Lambda_1(t) = \int_0^t \tilde{H}_{CSA}(t') dt' - t F_1 \quad (24)$$

This gives the following result:

$$\Lambda_1(t) = \frac{1}{2} \sum_i \sum_{n=-2}^{+2} f_n^i e^{-in\gamma^i} \left(\frac{1}{in\omega_R} \right) (e^{-in\omega_R t} - 1) (-I_X^i + I_Y^i) + \sum_i \sum_{m=-\infty}^{+\infty} \left(\frac{-1}{im\omega_R} \right) (e^{-im\omega_R t} - 1) e^{-im\gamma^i} \sum_{n=-2}^{+2} f_n^i a_{m-n} (I_X^i + I_Y^i) \quad (25)$$

This is the first order term of the argument of the time evolution with periodically time-dependent coefficients. A simple case can be study for numerical analysis by considering one spin system with $m = 1$, $\gamma^i = 0$. The function $\Lambda_1(t)$ is simplified as:

$$\begin{aligned} \Lambda_1(t) = & f_1 \left(\frac{-1}{i\omega_R} \right) (e^{-i\omega_R t} - 1) I_Y + \frac{1}{2} f_{-1} \left(\frac{1}{i\omega_R} \right) (e^{i\omega_R t} - 1) (-I_X + I_Y) + \\ & + f_2 \left[\left(\frac{-1}{i2\omega_R} \right) (e^{i2\omega_R t} - 1) (-I_X + I_Y) + \frac{1}{\pi\omega_R} (e^{-i\omega_R t} - 1) (I_X + I_Y) \right] + \\ & + f_{-2} \left[\left(\frac{1}{i2\omega_R} \right) (e^{i2\omega_R t} - 1) (-I_X + I_Y) - \left(\frac{1}{3\pi\omega_R} \right) (e^{-i\omega_R t} - 1) (I_X + I_Y) \right] \end{aligned} \quad (26)$$

Or writing this function in terms of the rotor period, $\omega_R = \frac{2\pi}{\tau_R}$, we have:

$$\begin{aligned} \frac{\Lambda_1(t)}{\tau_R} = & f_1 \left(\frac{-1}{4\pi i} \right) (e^{-i2\pi\phi} - 1) I_Y + f_{-1} \left(\frac{1}{4\pi i} \right) (e^{i2\pi\phi} - 1) (-I_X + I_Y) + \\ & + f_2 \left[\left(\frac{1}{8\pi i} \right) (e^{-i4\pi\phi} - 1) + \frac{1}{2\pi^2} (e^{i2\pi\phi} - 1) \right] I_X + \left(\frac{1}{8\pi i} \right) (e^{-i4\pi\phi} - 1) + (e^{-i2\pi\phi} - 1) \left(\frac{1}{2\pi^2} \right) I_Y \Big] + \\ & + f_{-2} \left[\left(\frac{-1}{8\pi i} \right) (e^{i4\pi\phi} - 1) - \frac{1}{6\pi^2} (e^{-i2\pi\phi} - 1) \right] I_X + \left(\frac{1}{8\pi i} \right) (e^{i4\pi\phi} - 1) - \frac{1}{6\pi^2} (e^{-i2\pi\phi} - 1) \Big] I_Y \end{aligned} \quad (27)$$

where the variable is chosen to be a dimensionless number $\phi = \frac{t}{\tau_R}$. The real, imaginary, and absolute parts of this function can be plotted versus the dimensionless number to get insight of the magnitude of the CSA in different orientation of the molecule. In this particular consideration, it appears that initially ($t = 0$, $\phi \rightarrow 0$) and at one rotor period ($t = \tau_R$, $\phi \rightarrow 1$),

the magnitude of the CSA is null which correspond to $\frac{\Lambda(0)}{\tau_R} = \frac{\Lambda(\tau_R)}{\tau_R} = 0$.

For $t = \frac{\tau_R}{2} \rightarrow \phi = \frac{1}{2}$, we have

$$\frac{\Lambda_1(\frac{\tau_R}{2})}{\tau_R} = f_1 \left(\frac{-1}{4\pi i} \right) (-2) I_Y + f_{-1} \left(\frac{1}{4\pi i} \right) (-2) (-I_X + I_Y) + f_2 \left[\frac{1}{2\pi^2} (-2) I_X + (-2) \left(\frac{1}{2\pi^2} \right) I_Y \right] + f_{-2} \left[\frac{-1}{6\pi^2} (-2) I_X - \frac{1}{6\pi^2} (-2) I_Y \right] \quad (28)$$

For $t = \frac{\tau_R}{4} \rightarrow \phi = \frac{1}{4}$, we have

$$\frac{\Lambda_1(\frac{\tau_R}{4})}{\tau_R} = f_1(\frac{-1}{4\pi i})(-2)I_Y + f_{-1}(\frac{1}{4\pi i})(i-1)(-I_X + I_Y) +$$

$$f_2 \left[\left(\frac{1}{8\pi i}(-2) + \frac{1}{2\pi^2}(i-1) \right) I_X + \left(\frac{1}{8\pi i}(-2) + \left(\frac{1}{2\pi^2} \right)(-i-1) \right) I_Y \right] + \quad (29)$$

$$f_{-2} \left[\left(\frac{-1}{8\pi i}(-2) - \frac{1}{6\pi^2}(-i-1) \right) I_X + \left(\frac{1}{8\pi i}(-2) - \left(\frac{1}{6\pi^2} \right)(-i-1) \right) I_Y \right]$$

These instantaneous values of $\frac{\Lambda_1(t)}{\tau_R}$ means that the magnitude of the CSA in different orientation of the molecule depends on the orientation of the molecule and on the CSA tensor elements.

III. Discussion and Conclusion

The two seminal approaches (AHT, FLT) bear similarities to the newly introduced FME approach in that all the three approaches use an expansion of the evolution operator into orders of decreasing importance. The AHT propagator is given by:

$$U(t_c) = \exp \left\{ -i\bar{H}(t_c)t_c \right\}, \quad (30)$$

where $\bar{H}(t_c)$ is the average Hamiltonian and t_c corresponds to the period of a periodic Hamiltonian $H(t)$. The FLT propagator is given by:

$$U(t) = P(t) \cdot \exp \{ -iH_F t \}, \quad (31)$$

where the operator $P(t)$ is periodic with the period t_c while the Floquet Hamiltonian H_F is time-independent. The connection of FLT to AHT is apparent by setting,

$$P(0) = P(nt_c) = 1, \quad (32)$$

and by assuming stroboscopic observation which shows the identity

$$H_F = \bar{H}. \quad (33)$$

The FME propagator is given by:

$$U(t) = P(t) \exp \{ -itH_F \} P^\dagger(0). \quad (34)$$

Here the constraint of stroboscopic observation is removed. $P(t)$ is the operator that introduces the frame that varies under the time independent Hamiltonian H_F . The function $\Lambda(t)$ given explicitly above is the argument of the operator $P(t)$ such that:

$$P(t) = \exp \{ -i\Lambda(t) \}. \quad (35)$$

However, the Fer expansion expresses the propagator in the form of an infinite-product of a series of exponentials given by:

$$U(t) = \prod_{k=1}^{\infty} \exp \{ H_{F_k}(t) \} = \exp \{ H_{F_1}(t) \} \exp \{ H_{F_2}(t) \} \dots \quad (36)$$

All these propagators are dictated by the Schrodinger picture Liouville-von Neumann equation of motion:

$$i\frac{dU}{dt}=H(t)U(t). \quad (37)$$

We have made a brief overview of the AHT and FLT which have been used extensively to analyze various experiments in quantum physics in general and solid-state NMR in particular and have been successful for designing sophisticated pulse sequences and understanding of different experiments. I present two developing and emerging theories in solid-state NMR (FME, FE). The combinations of two or more of the theories described therein will provide a framework for treating time-dependent Hamiltonian in NMR in a way that can be easily extended to both synchronized and several nonsynchronized modulations. With the increase of the level of sophistication of NMR experiments, second and third order terms are of increasing importance, such as in diffusion experiment. The intention of writing this brief historical overview of the two major theories in NMR and the developing ones is to help bring the current and future prospective theoretical aspects of spin dynamics in NMR to the attention of the NMR community and lead new interactions between nuclear magnetic resonance experts and specialists⁴⁵. An extremely important point to tackle and now developing is the possibility of enhanced the performance of the FME approach in order to bring out the salient features of the scheme and explore its use in the spin dynamics NMR community. Additional quantitative work will demonstrate further utility of the Floquet-Magnus expansion in nuclear magnetic resonance, in spin physics and in many other areas.

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Appendix

The time-dependent Fourier coefficients can be written as following:

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

Written the coefficients in the first and second half of the sequence respectively as follows:

$$a_k^X = \frac{1}{\tau_R} \int_0^{\tau_R/2} e^{ik\omega_R t} dt \quad (39)$$

and

$$a_k^Y = \frac{1}{\tau_R} \int_{\tau_R/2}^{\tau_R} e^{ik\omega_R t} dt \quad (40)$$

We explicitly obtain:

$$a_0^X = a_0^Y = \frac{1}{2}, \quad (41)$$

$$a_k^X = -a_k^Y = a_k = \frac{1}{2\pi i k} (e^{ik\pi} - 1). \quad (42)$$

The toggling frame is rewritten as

$$\begin{aligned} \tilde{H}_{CSA}(t) &= \sum_i \delta_{CSA}^i(t) I_Y^i \left(\sum_n a_n e^{-in(\omega_R t + \gamma)} \right) - \sum_i \delta_{CSA}^i(t) I_X^i \left(1 - \sum_n a_n e^{-in(\omega_R t + \gamma)} \right) \\ &= \sum_i \delta_{CSA}^i(t) I_Y^i \left(a_0 + \sum_{k \neq 0} a_k e^{-ik(\omega_R t + \gamma)} \right) - \sum_i \delta_{CSA}^i(t) \left(a_0 - \sum_{k \neq 0} a_k e^{-ik(\omega_R t + \gamma)} \right) I_X^i \\ &= \sum_i \delta_{CSA}^i(t) a_0 (-I_X^i + I_Y^i) + \sum_i \delta_{CSA}^i(t) \sum_{k \neq 0} a_k e^{-ik(\omega_R t + \gamma)} (I_Y^i + I_X^i) \end{aligned} \quad (43)$$

Introducing eq. (14) into eq. (43), we have

$$\tilde{H}_{CSA}(t) = \frac{1}{2} \sum_i \sum_{n=-2}^{+2} f_n^i(\alpha, \beta, \sigma^i) e^{-in(\omega_R t + \gamma)} (-I_X^i + I_Y^i) + \sum_i \sum_{n=-2}^{+2} f_n^i(\alpha, \beta, \sigma^i) e^{-in(\omega_R t + \gamma)} \sum_{k \neq 0} a_k e^{-ik(\omega_R t + \gamma)} (I_X^i + I_Y^i) \quad (44)$$

Arranging terms, we have

$$\tilde{H}_{CSA}(t) = \frac{1}{2} \sum_i \sum_{n=-2}^{+2} f_n^i(\alpha, \beta, \sigma^i) e^{-in(\omega_R t + \gamma)} (-I_X^i + I_Y^i) + \sum_i (I_X^i + I_Y^i) \sum_{n=-2}^{+2} f_n^i(\alpha, \beta, \sigma^i) \sum_{k \neq 0} a_k e^{-i(n+k)(\omega_R t + \gamma)} \quad (45)$$

Setting $m = n + k$, we have

$$\tilde{H}_{CSA}(t) = \frac{1}{2} \sum_i \sum_{n=-2}^{+2} f_n^i(\alpha, \beta, \sigma^i) e^{-in(\omega_R t + \gamma)} (-I_X^i + I_Y^i) + \sum_i (I_X^i + I_Y^i) \sum_{n=-2}^{+2} f_n^i(\alpha, \beta, \sigma^i) \sum_{m=-\infty}^{+\infty} a_{m-n} e^{-im(\omega_R t + \gamma)} \quad (46)$$

Next,

$$\tilde{H}_{CSA}(t) = \frac{1}{2} \sum_i \sum_{n=-2}^{+2} f_n^i(\alpha, \beta, \sigma^i) e^{-in(\omega_R t + \gamma)} (-I_X^i + I_Y^i) + \sum_i (I_X^i + I_Y^i) \underbrace{\sum_{n=-2}^{+2} f_n^i a_{-n}}_{AHT = \bar{f}_n^i} + \sum_i (I_X^i + I_Y^i) \sum_{n=-2}^{+2} f_n^i \sum_{m=-\infty}^{+\infty} a_{m-n} e^{-im(\omega_R t + \gamma)} \quad (47)$$

Using eq. (42), we can write the following

$$a_{-n} = \frac{-1}{2\pi i n} (e^{-in\pi} - 1) \quad (48-a)$$

$$a_{-1} = -a_1 = \frac{1}{\pi i} \quad (48-b)$$

$$a_2 = a_{-2} = 0 \quad (48-c)$$

$$a_0 = \frac{1}{2} \quad (48-d)$$

HIGHLIGHTS

- Various theories in solid-state NMR.
- Application of FME to CSA when irradiated by BABA pulse sequence
- Criterion for the CSA to be averaged out

Fig. 1.

Solid echo pulse sequence for refocusing the quadrupolar Hamiltonian. The two $\frac{\pi}{2}$ phase shifted pulses are separated by a delay $\tau - 2\alpha$, where 2α is the $\frac{\pi}{2}$ pulse width. The phases (x, y) of the two-pulses shown can be any combination of phase shifted 90 degree pulses.

Fig. 2. Absolute value of the difference of the observable single quantum (SQ) coherences for spin $I=1$ as predicted by first-order AHT and that from a numerical solution to the VN equation for the pulse sequence shown in Fig. 1 for different values of τ .

Fig. 3. Absolute value of the difference of the observable single quantum (SQ) coherences for spin $I=3/2$ as predicted by first-order AHT and that from a numerical solution to the VN equation for the pulse sequence shown in Fig. 1 for different values of τ .

Fig. 4.

Absolute value of the difference of the observable single quantum (SQ) coherences for spin $I=5/2$ as predicted by first-order AHT and that from a numerical solution to the VN equation for the pulse sequence shown in Fig. 1 for different values of τ .

Fig. 5.
Numerical function of finite Pulse BABA sequence