**Physical Sciences**

**Advances in Theory of Solid-State Nuclear Magnetic Resonance**

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Recent advances in theory of solid state nuclear magnetic resonance (NMR) such as Floquet-Magnus expansion and Fer expansion, address alternative methods for solving a time-dependent linear differential equation which is a central problem in quantum physics in general and solid-state NMR in particular. The power and the salient features of these theoretical approaches that are helpful to describe the time evolution of the spin system at all times are presented. This review article presents a broad view of manipulations of spin systems in solid-state NMR, based on milestones theories including the average Hamiltonian theory and the Floquet theory, and the approaches currently developing such as the Floquet-Magnus expansion and the Fer expansion. All these approaches provide procedures to control and describe the spin dynamics in solid-state NMR. Applications of these theoretical methods to stroboscopic and synchronized manipulations, non-synchronized experiments, multiple incommensurated frequencies, magic-angle spinning samples, are illustrated. We also reviewed the propagators of these theories and discussed their convergences. 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. *Journal of Nature and Science, 1(6):e109, 2015*

I. Introduction

In his famous speech “There’s plenty of room at the bottom”, given on December 29th 1959 at the annual meetings of the American Physical Society at Caltech, the quantum physicist, Richard Feynman raised the problem of manipulations and controlling things on a small scale [1]. At that time, several branches of science were still independent with little shared interest. Physicists often commented to biologists: “you know the reason you fellows are making so little progress, you should use more mathematics like we do.” One can speculate that view was valid and well received in the 1950’s, because today biology is a field that has seen more rapid progress than any other scientific fields [1,2,3]. The collaboration between biologists and physicists paved the way for new scientific branches that have perhaps been among the most active fields of science for more than half a century. These biological and bio-chemical disciplines aim to understand the molecular basics of the microscopic aspects of living organisms. For the study of molecular geometry of many different phases of matter and for molecular dynamics, nuclear magnetic resonance spectroscopy has proven to be very successful and versatile.

Spectroscopy is an invaluable technique that serves various field of science. Of the various spectroscopic methods the technique of nuclear magnetic resonance (NMR) remains much a vibrant field of research due to its theoretical components from outstanding scientists. The technique of NMR is well-established and has been driven by exciting and developing theoretical contributions from quantum physicists and mathematicians [3-19,21-113].

Given the apparent simplicity of basic nuclear magnetic resonance experiments, a naïve spectroscopist might wonder how NMR remains a vibrant field of research after nearly 70 years of contributions from scientists. The two main answers are quantitative improvements in magnetic resonance (technological advances), and qualitative improvements. Qualitative improvements come from the possibilities of manipulating spin evolutions which can be accurately described by quantum mechanics and mathematics, and the abundance of physical, chemical and biological systems containing spins ($I \neq 0$) that produce NMR signals, and specific physical and chemical environments for the spins.

Since its earliest developments in the 1940s [4,5], NMR has grown into a technique of great richness, especially with solid-state NMR. Much progress has been made in the application of solid-state NMR to elucidate molecular structure and dynamics in systems not amenable to characteristics by any other way. The importance of solid-state nuclear magnetic resonance stands in its ability to accurately determine intermolecular distances and molecular torsion angles [7-10]. In NMR spectroscopy, spectra obtained from solids are broader and much more complex compared to that of liquids. In liquids, rapid isotropic motions of the nuclei average out the anisotropic interactions effectively to zero, whereas in the case of solids, these interactions are not averaged out [11-17].

The technique of NMR spectroscopy deals with time-dependent interactions of nuclear spins system and it is imperative to solve the time-dependent Schrödinger equation in order to understand and predict the spin system dynamics. Solving time-dependent linear

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differential equations is a central problem in quantum physics in general and solid-state NMR [18]. Several theories have been developed and introduced to solid-state NMR. Among these approaches, the average Hamiltonian theory (AHT) [19] and Floquet theory (FLT) [20-23] are the most widely used theories in the NMR literature. The first (AHT) explains how periodic pulse sequence can be used to switch off or transform the symmetry of selected interactions in coupled, many spin systems allowing NMR spectroscopists to create effective spin Hamiltonians with a wide variety of intriguing and useful properties [24-37]. The second (FLT), unlike AHT, is not limited to stroboscopic observation. The Floquet theory has proven to be a powerful tool for the spin system under periodical time-dependent Hamiltonians such as solid samples undergoing mechanical rotations at the magic-angel, or solution samples subjected to cyclic RF irradiation. This approach (FLT) has the advantage of describing the spin dynamics at all times and it is not limited to a single time-dependent perturbation, but valid for cases subjected to interactions with multiple time periodicities [38-61].

The ultimate goal of this review paper is deliberately to downplay the evolution of theories used in solid-state nuclear magnetic resonance, from the milestone theories including the AHT and the FLT to the most recent theories such as the Floquet Magnus expansion (FME) [18] and the Fer expansion (FE) [62,63]. The theory of FME is a unique approach in spin dynamics that shed new lights on AHT and FLT. This scheme was recently introduced to solid-state NMR, and applied to many NMR interactions [18,64-67]. The other developing approach in NMR community is the FE expansion [63]. This approach is still in its infancy and was illustrated in NMR by considering simple applications such as the calculation of Bloch-Siegert shift in NMR and the analyzing of the heteronuclear decoupling in solid-state NMR [62].

This paper discusses major milestones theories including average Hamiltonian theory and the Floquet theory. Next emerging theories, including Fer expansion and Floquet-Magnus expansion, are covered. Various illustrative applications highlighting the potential of these theories in analyzing a variety of solid-state NMR experimental methods are presented. Our conclusions present the propagators and discuss the convergence aspects of the theories therein.

II. Milestones Theories
II.1. Average Hamiltonian Theory
An important landmark to describe the effect of time-dependent interactions and the accompanying improvements was the introduction of average Hamiltonian theory (AHT) in NMR. Developed by John Waugh and co-workers in 1968, the AHT approach became the main tool to study the dynamics of spin systems subject to an RF perturbation. This approach is the most commonly used method to treat theoretical problems in solid-state NMR and have been used sometimes casually [68]. The AHT 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 involves considering a time dependent Hamiltonian $H(t)$ governing the spin system evolution, and describing 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 [26,44].

This technique has been widely used in the NMR literature in the development of multiple pulse sequences and in the context of both decoupling and recoupling experiments. 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 train.

II.1.1 The Magnus expansion
The Magnus expansion [44, 69-85] was first applied to NMR in 1968 by Evans [69] and Haeblerien and Waugh [19]. Since that time, the ME has been instrumental in the development of improved techniques in NMR spectroscopy [44,70]. On a personal note, Blanes et al. [74] provided the following solution of the Magnus expansion to the initial value problem,

$$\frac{dY}{dt} = Z(t)Y(t), \quad Y(t_0) = Y_0, \quad t \in \mathbb{R}, \quad Y(t) \in \mathbb{C}^n, \quad Z(t) \in \mathbb{C}^{n \times n},$$ (1)

in terms of exponentials of combinations of the coefficient matrix $Z(t)$. Eq. (1) is a first order linear homogeneous system of differential equations in which $Y(t)$ is the unknown $n \times n$-dimensional vector function. In general, $Y_0$, $Y$ and $Z(t)$ are complex-valued. The scalar case, $n = 1$, has the general solution

$$Y(t) = \exp\left(\int_{t_0}^{t} Z(t')dt'\right)Y_0.$$ (2)

This expression is still valid for $n > 1$ if the matrix $Z(t)$ is constant; or the commutator $[H(t_1), H(t_2)] = 0$, for any pair of values of $t_1$ and $t_2$. In general, there is no compact formula for the solution of Eq. (1) and the Magnus proposal endeavor to complement Eq. (2) in the following direction. If a term is added to the argument in the exponential such as

$$Y(t) = \exp\left(\int_{t_0}^{t} Z(t')dt' + M(t,t_0)Y_0 \right),$$ (3)

then the Magnus expansion provides $M(t,t_0)$ as an infinite series. A salient feature of the Magnus expansion is the fact that, when $Z(t)$ belong to a given Lie algebra, if we express $Y(t) = U(t,t_0)Y_0$, then $U(t,t_0)$ belong to the corresponding Lie group. By construction, the Magnus expansion lives in the Lie algebra. Furthermore, this is also true for their truncation to any order. In many applications this mathematical setting reflects important features of the problem. This pure mathematics terminology can be related to NMR by setting the coefficient matrix, $Z(t) = -iH(t)$. The operator $U(t,t_0)$ is the propagator which satisfies the time-dependent Schrödinger equation, $\frac{dU}{dt} = -iH(t)U(t),$ which is a differential equation. The time-dependent Schrödinger equation is difficult to be solved unless $H$ is time-independent or commutes with itself at two different times [28,29]. As highlight by Madhu and co-worker [62], in most cases, when that is not the case, attempt is made to represent the evolution of the system in terms of an operator that is representative of the overall evolution of the system. This could be an effective Hamiltonian or an effective propagator. The Magnus expansion has been successfully applied as a perturbative tool in numerous areas of physics and chemistry such as in nuclear magnetic resonance. The Magnus expansion has been systematically used in NMR, in particular in solid-state NMR where it forms the basis of AHT.

II.1.2 Useful equations
The main result of AHT is given by [19,26,34-36]

$$\bar{H}_0 = \bar{H}_0^{(0)} + \bar{H}_0 + \bar{H}_0^2 + ...$$ (4)
with
\[ \tilde{H}_0(t) = \frac{1}{t_c} \int_0^{t_c} dt_i \tilde{H}_0(t_i), \]
\[ (5) \]
\[ \overline{H}_0^{(1)} = -\frac{1}{2t_c^2} \int_0^{t_c} dt_i \int_0^{t_c} dt_i \left[ \tilde{H}_0(t_2), \tilde{H}_0(t_1) \right], \]
\[ (6) \]
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 expansion which forms the basis of AHT.

II.1.3 Applications
The method of AHT has been gradually applied to many theoretical problems in solid-state NMR [68]. Here we present some applications we recently performed.

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:

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 \( t - \alpha \), a \( \frac{\pi}{2} \) pulse about \( Y \) axis, followed by two spin locking fields of duration \( 2t - \alpha \), and ending with the application of a second \( \frac{\pi}{2} \) pulse about \( Y \) axis. This 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., \( \mu s \) to \( 10 s \)). This is in contrast to quadrupolar echo sequence where efficient line-narrowing is obtained when using very short free evolution times (typically less than \( 10 \mu s \)). 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. [34]. 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 [33-35,99,112,113]. Fig. 3 also represents the magic echo sequence for refocusing the quadrupolar interaction. In the following subsections, we investigated various interactions in solid-state NMR when irradiated with the magic echo pulse sequence. We have neglected J coupling in this paper and all the duration of the \( \frac{\pi}{2} \) pulses are \( 2\alpha \). We consider only the first-order quadrupolar coupling and neglect all the secular components from the second and upper-order.
where $2 \Delta \alpha$ is the duration of $\frac{\pi}{2^2}$ pulse width, and $\omega_D$ is the dipolar coupling constant. $\omega_{RF}$ is the RF field strength, $\Delta \omega$ is the resonance offset, and $\omega_Q$ 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 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 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 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 Pines has been used. Note that, the zero-order term of the average Hamiltonian for the quadrupolar interaction (Eq. (9)) is obtained when using the magic echo sequence with a $\frac{\pi}{2}$ pulse about x axis inserted during the first free evolution time as in the figure (Fig. 3) showed in the work by Mananga et al [34].

II.1.4 Advantages and limitations

AHT cannot properly describe some experimental results where the effects of second-and higher-order truncated interactions are not negligible. For instance, the time evolution is eventually controlled by higher-order effects due to non-secular terms [68,116]. Several authors had explored the case of discrepancies arising in the average Hamiltonian of the anisotropies due to second-order effects when a quadrupolar coupling becomes comparable to the Zeeman interaction [68]. The simulation and experimental results performed by Goldman and co-workers show a failure of AHT, while an analysis based on static perturbation theory (SPT) is in good agreement throughout the range of experimental parameters. It is important to note that, the SPT computation includes second order effects but neglects all geometric effects. An interesting quotation of Goldman [68] was that: “because of its natural formulation in terms of irreducible tensor expressions, AHT has been gradually applied to almost every kind of situation, sometimes abusively”. AHT is not applicable to Hamiltonians with multiple basic frequencies [38,39]. No single cycle time can be defined if the two frequencies are incommensurate: MAS and radiofrequency irradiation must be synchronized or time-scale separated, multiple irradiations must be synchronized or time-scale separated. Only stroboscopic observation is allowed after a full cycle time. The Nyquist frequency equals the basic frequency while side bands appear at integer multiples of the basic frequency. Sidebands in MAS spectra cannot be described and are folded back onto the center band. Sidebands in rf irradiation schemes are neglected and folded back onto the center band. Convergence of the series expansion of the Hamiltonian can be a problem. Usually the basic sequence expansion has to be larger than the transition frequencies in the Hamiltonian. The AHT holds well for statics experiments while also it presents several failures described in the references [26,38,39,105,108-111]. Some NMR experiments, such as simple rotation and pulse crafting are more conveniently described by Floquet theory. In addition, the application of AHT requires defining a single basic frequency as well as a cycle time of the Hamiltonian. AHT failed to explain phenomena of heteronuclear decoupling, which involves multiple spins in the form of strongly coupled protons in addition to the observed nuclei.

Recently, the validity of the AHT method was probed for quadrupolar nuclei [36]. 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. 2, Mananga et al. [36] have shown that the ability of the AHT to predict the spin dynamics depends on the size of the spin system.

II.2. Floquet Theory

The FLT introduced to the NMR community in the early 1980’s simultaneously by Vega [23] and Maricq [22] 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 expansion. The theory maps the finite-dimensional time-dependent Hilbert space onto an infinite-dimensional but time-independent Floquet space [38-61]. 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 anisotropy of sample properties. The FLT has been applied satisfactorily to simple-spin systems, spin-pair systems to study important NMR phenomena including rotational-resonance, composite pulse sequence designing, field-dependent chemical shifts, cross-polarization dynamics, two-dimensional solution NMR experiments, and the dynamic characteristics of exchanging spin systems. The general description of the FLT is equally applicable to dipolar systems as well as to quadrupolar nuclear spin systems. However, spin systems with large quadrupolar couplings may violate the convergence conditions for the expansions employed to evaluate the Floquet matrices. An important question to answer is 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 [36]. 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 impractical. Analytical calculations are limited to small spin systems and it is difficult to get physical insight from matrix representation [94,100]. For instance, Matti Maricq obtained results that show 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 [22,26].

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 multi-mode Floquet calculations can become intractable. Massive reduction in dimensionality by truncation of the Fourier dimensions can introduce artifacts. In the literature, problems with four frequencies have been studied recently [114]. Meier’s group [114] investigated third-spin assisted heteronuclear recoupling experiments, which play an increasingly important role in measuring long-range heteronuclear couplings, in particular $^1\text{H}-^3\text{C}$, in proteins. The proton-assisted insensitive nucleus cross-polarization (PANCP) experiment described has to take into account the four frequencies that modulate the interaction-frame Hamiltonian: the MAS frequency and the three nutation frequencies corresponding to the rf-field amplitudes of the three spin-lock fields [114]. Such a time-dependent Hamiltonian can be analyzed in the framework of operator-based Floquet theory [38,39] to obtain effective Hamiltonians. Furthermore, the demand of experiments that require
four frequencies for a full description is increasing. For instance, non-cyclic multiple-pulse sequences like two-pulse phase-modulated (TPPM) decoupling experiment acquire four frequencies under double rotation (DOR) and there are some other obvious problems with four frequencies like triple-resonance CW radio frequency irradiation under MAS.

II.2.1 Useful equations

II.2.1.1 Operator-based Floquet theory

Operator-based Floquet theory in solid-state NMR was extensively and explicitly described in the literature of solid-state NMR including the articles by M. Leskes et al. [38], I. Scholz et al. [39], and S. Vega [100]. The following results are extracted from their work.

Single-mode Floquet Hamiltonian: a periodic time-dependent Hamiltonian can be expanded in a Fourier series of the form,

$$\hat{H}(t) = \sum_{\omega_m} (a) \hat{H} e^{i\omega_m t}$$

where \(\omega_m\) is the characteristic frequency. The operators \((a)\hat{H}\) can be viewed as Fourier coefficients of the Hamiltonian with respect to this frequency. The effective Hamiltonian for a single-mode Floquet Hamiltonian can be obtained to different orders given by

$$\overline{\hat{H}} = \left[ \sum_{n_0=0}^\infty \frac{1}{2\pi a} \sum_{n=-\infty}^{\infty} \left( n_0 + k_0 \right) \hat{H} e^{i\omega_m t} e^{i\kappa n_0 t} \right] + \ldots$$

where \(n_0, \omega_m, \kappa\) are the characteristic frequencies. The operators \((a,\kappa)\hat{H}\) can be viewed as Fourier coefficients of the Hamiltonian with respect to these frequencies. The effective Hamiltonian for a single-mode Floquet Hamiltonian can be obtained to different orders given by

$$\overline{\hat{H}} = \sum_{n_0=0}^\infty \sum_{n=-\infty}^{\infty} (a,\kappa) \hat{H} e^{i\omega_m t} e^{i\kappa n_0 t}$$

with \(n_0, \omega_m, \kappa\) and \(\omega_m + \kappa n_0 \neq 0\).

For bimodal Floquet problem, resonance phenomena will always involve both frequencies.

Bimodal Floquet Hamiltonian: a periodic time-dependent Hamiltonian can be expanded in a Fourier series of the form

$$\hat{H}(t) = \sum_{\omega_m, \omega_p} \sum_{\omega_p=0}^\infty \sum_{\kappa=-\infty}^{\infty} \left( n_0 + k_0 + k_p \right) \hat{H} e^{i\omega_m t} e^{i\kappa n_0 t} e^{i\omega_p t}$$

where \(\omega_m\), \(\omega_p\), and \(\kappa\) are the characteristic frequencies. The operators \((a,\kappa)\hat{H}\) can be viewed as Fourier coefficients of the Hamiltonian with respect to these frequencies. The effective time-independent Hamiltonian for a triple-mode Floquet Hamiltonian can be obtained to different orders given by

$$\overline{\hat{H}} = \sum_{n_0=0}^\infty \sum_{n=-\infty}^{\infty} \sum_{n_p=-\infty}^{\infty} \left( n_0 + k_0 + k_p \right) \hat{H} e^{i\omega_m t} e^{i\kappa n_0 t} e^{i\omega_p t}$$

with \(n_0, \omega_m, \kappa n_0 \neq 0\).

II.2.2 Applications

Several MAS NMR experiments on spin systems with a periodically time-dependent Hamiltonian were extensively discussed in the recent articles by Leskes et al. [38] and Scholz et al. [39]. For many MAS NMR experiments, understanding the spin dynamics requires a wise choice of the interaction frame in which the Hamiltonian is presented. A transformation of the Hamiltonian to such a frame often leads to periodic time dependences which can be removed by an additional transformation to the Floquet representation. After deriving the Floquet Hamiltonian, the van Vleck transformation was applied to obtain an effective Hamiltonian. Leskes et al. [38] and Scholz et al. [39], applied Floquet theory to investigate numerous cases such as MAS, rotational-resonance recoupling, CW irradiation on a single spin species, DARR and MIRROR recoupling, phase-alternating (XiX) irradiation on a single spin species, CW irradiation on one and XiX irradiation on a second spin species, phase-modulated Lee-Goldburg decoupling, C-type and R-type sequences, TPPM decoupling, CSA spectra during MAS experiments, recoupling under MAS (rotational resonance, recoupling and decoupling with CW irradiation), heteronuclear decoupling, cross polarization, homonuclear decoupling, quadrupolar nuclei, and dynamic MAS. Scholz, van Beek, and Ernst extensively described the case of CW decoupling under MAS [39]. The authors assumed a two-spin system, I-S with rf irradiation on the I spin. The Hamiltonian describing this system, in the rotating frame, is given by

$$\hat{H}(t) = \sum_{k=2}^{\infty} \sum_{s=0}^{2} \sum_{s=0}^{2} \sum_{s=0}^{2} \left( \omega_s \right) e^{i\omega_s t} S_{s} I_{s} e^{i\omega_s t}$$

The coordinate system of the I spin is tilted by 90° around the z axis such that the rf is along the z axis. The transformation into an interaction frame with the rf gives

$$\hat{H}(t) = e^{i\omega t} \hat{H}(t) e^{-i\omega t}$$

(20)
\( \tilde{H}(t) = \sum_{n=1}^{2} \omega_n e^{i \omega_n t} S_z - \sum_{n=1}^{2} \omega_n e^{i \omega_n t} \left( \frac{1}{2} I^x e^{i \omega t} + \frac{1}{2} I^y e^{-i \omega t} \right) \)  
(22)

The Fourier coefficients of the above Hamiltonian \( \tilde{H}(t) \) can be written:

\( \tilde{H} = \omega_0 S_z \)  
(23)

\( \tilde{H} = \omega_1 S_z \)  
(24)

\( \tilde{H} = -\frac{\omega_0}{2} I^z - \omega_1 S_z I^z \)  
(25)

\( \tilde{H} = -\frac{\omega_0}{2} I^z - \omega_1 S_z I^z \)  
(26)

\( \tilde{H} = 0 \)  
(27)

The first index describes the rotation in real space (MAS) while the second index describes the rotation in spin space (interaction frame).

II.2.3 Advantages and limitations

The Floquet description in which the field energy has no lower bound is valid only in the limit of large photon numbers, as in NMR applications. Spontaneous-emission effects cannot be obtained [101]. Comparing the Floquet theory and AHT results, Llor [101] found a supplementary non-secular term that appears in the second-order effective Hamiltonian. Llor presented the general equivalence between the AHT and the Floquet theory which tell that the choice between these methods is just a matter of convenience, depending, for instance, on the type of time modulation of the Hamiltonian [101]. To this end, theoretical treatments such as Floquet theory and secular averaging theory could be employed with suitable modifications as alternatives to AHT for describing the underlying dynamics in MAS experiments. Although the Floquet approach describes the time evolution of the spin system under a time-independent Hamiltonian, the infinite dimensionality involved in the description often complicates its practical application in solid-state NMR. Thus, the time-dependent problem is transformed to a time-independent but infinite-dimensional problem [38,39,60,61,68,101,102].

The Floquet theory can manipulate multiple incommensurate frequencies. In the NMR literature, Floquet theory has treated problems with up to four frequencies and there are several experiments that require more frequencies for full description [114]. The Floquet description needs an additional Fourier space to describe the quantization of the motional process. This theory is an exact method and does not imply any assumptions or approximations. The expressions of the effective Hamiltonian in the spin-Hilbert space without detailed knowledge of the structure of the spin Hamiltonian can be calculated. Results of the operator-based Floquet theory are given above in the useful equations’ subsection (II.2.1).

Operator-based Floquet theory can easily be expanded to multiple incommensurate frequencies with expressions that are independent of the detailed structure of the spin-Hilbert-space Hamiltonian leading to an effective Hamiltonian that can be written as an analytical operator expression. The operator-based Floquet theory can be used to treat systems with many spins as long as the commutators can be calculated, but this operator cannot treat resonance conditions that involve simultaneous transition in Fourier space and spin space. Matrix-based Floquet description leads to an accurate description of time-dependent Hamiltonians including the sidebands and they can be combined with perturbation theory to get insight into processes that involve combined Fourier-space and spin-space resonance conditions. It is very difficult to get physical insight from the matrix representation and analytical calculations are limited to small spin systems. For multi-mode Floquet calculations, matrices can become very large, hence require truncation of the Fourier dimensions which introduce artifacts. In the numerical simulations, time slicing of the time-dependent Hamiltonian is almost always faster and simpler to implement. The problems associated with operator-based Floquet theory include; the observation limitation for resonance conditions that involve simultaneous transition in Fourier space and the spin space that cannot be treated. Also with operator-based Floquet theory, the sidebands cannot be obtained.

The development of alternatives theories such as the FME and the Floquet theory are necessary. For instance, the convergence of the Floquet expansion is much faster than that of Magnus expansion and is well defined [62]. Furthermore, the computation of the infinite numbers of commutators in the corrected Hamiltonian turn out to be simpler to manipulate in most experiment due to the fast convergence and the negligible value of many of the commutators. The FME provides a more concise and intuitive approach than Floquet theory.

III. Emerging Theories

III.1 Floquet expansion

The Floquet expansion was introduced recently to the NMR community by Madhu and Kurur [62] via the effect of Bloch-Siegert shift and heteronuclear dipolar decoupling [97,98]. This new approach in the field of NMR was formulated more than half a century ago by Fer [63]. This theory is another alternative expansion scheme for solving the time-dependent Schrodinger differential equation. Indeed, from the point of view of physical applications, the Magnus expansion has been extensively used in a variety of issues, while the Fer expansion has been either ignored or misquoted until recently [73]. This approach of FE is still in its infancy and can be considered to be complimentary to the Magnus expansion (AHT). While the efficiency of Floquet 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.

Similarly, as described for the Magnus expansion, Blanes et al. [74] provided also the following mathematics solution to the Fer expansion of the initial value problem.

\[ dY \frac{d}{dt} = Z(t)Y(t) , \quad Y(t_0) = Y_0 , \quad t \in \mathbb{R} , \quad Y(t) \in \mathbb{C}^n , Z(t) \in \mathbb{C}^{n \times n} , \]  
(1)

in terms of exponentials of combinations of the coefficient matrix \( Z(t) \). As above described, Eq. (1) is a first order linear homogeneous system of differential equations in which \( Y(t) \) is the unknown \( n \)-dimensional vector function. In general, \( Y_0 \), \( Y \) and \( Z(t) \) are complex-valued. The scalar case, \( n = 1 \), has the general solution

\[ Y(t) = \exp(-\int_{t_0}^{t} dH(t') dt') Y_0 \]  
(28)

This expression is still valid for \( n > 1 \) if the matrix \( Z(t) \) is constant and the commutator

\[ [H(t_1), H(t_2)] = 0 \]  
(29)

for any pair of values of \( t_1, t_2 \). In general, there is no compact formula for the solution of Eq. (1) and the Fer proposal...
endeavor to complement Eq. (28) in the following direction: If we attach a matrix factor to the exponential,

\[ Y(t) = \exp\left(-\int_{t_0}^{t} iH(t')dt\right)M(t, t_0)Y_0 \]  

(30)

then the Fer expansion gives an iterative multiplicative prescription to find \( M(t, t_0) \). A salient feature of Fer expansion stems from the fact that, when \( Z(t) \) belong to a given Lie algebra, if we express \( Y(t) = U(t, t_0)Y_0 \), then \( U(t, t_0) \) belong to the corresponding Lie group. By construction, the Fer expansion lives in the Lie group. Furthermore, this is also true for their truncation to any order. As described for the Magnus expansion, the connection between the mathematics terminology and the NMR can be made by setting the coefficient matrix to be \( Z(t) = -iH(t) \). In many applications this mathematical setting reflects important features of the problem.

III.1.1 Useful equations

The formalism of Fer expansion expresses the solution to the differential time-dependent Schrödinger equation in the form of an infinite-product of series of exponentials as [62]

\[ U(t) = \prod_{k=1}^{\infty} e^{F_k(t)} = e^{F_1(t)}e^{F_2(t)}... \]  

(31)

A knowledge of the Hamiltonian allow an easy evaluation of

\[ F_1 = \int_{0}^{t} dt' H(t') \]  

(32)

and

\[ H_F^{(0)} = e^{-F_1(t)}H e^{F_1(t)} - \frac{1}{2} \int_{0}^{t} dx e^{-F_1(x)}H e^{F_1(x)} \]  

(33)

The following iterative formula were derived

\[ F_n = -i\int_{0}^{t} dt'H^{(n-1)}(t'), \quad H_F^{(0)} = H, \quad H_F^{(n)} = \frac{1}{2} \left[ F_n, H_F^{(n-1)} \right] + \frac{1}{3} \left[ F_n, \left[ F_n, H_F^{(n-1)} \right] \right] + ... \]  

(34)

\[ H_F^{(n)} = \frac{-1}{2} \left[ F_n, H_F^{(n-1)} \right] + \frac{1}{3} \left[ F_n, \left[ F_n, H_F^{(n-1)} \right] \right] + ... \]  

(35)

where \( n = 1, 2, 3, ... \). Therefore, the Fer expansion involves a series of nested commutators resulting in \( H_F^{(n)} \). The Fer expansion differs to the Magnus approach in the form of the correction terms. 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 series 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:

\[ \frac{F_1(\tau_C)}{\tau_C} = \overline{H} \]  

(36)

where \( \tau_C \) 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 \( F_1(t) \) 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. Blanes et al. [44,73,75,78] had proved the convergence of the Fer expansion and showed that the convergence of Fer expansion is much faster than that of Magnus expansion. Madhu and Kurar [62] also highlighted the observations such that the calculation of a term like \( \overline{H} \) will contain several of the important signatures of the various higher-order terms in Magnus expansion, where all terms 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 Schrödinger equation:

\[ \frac{dU}{dt} = -iH(t)U(t) \]  

(37)

III.1.2 Advantages and limitations

The Fer expansion [88-93] is an elegant expansion scheme involving the product of exponentials for the calculation of effective propagators and effective Hamiltonians in time-dependent problems which are of common occurrences in solid-state NMR. Unlike in the Magnus expansion where an evaluation of nested commutators and their integrals are required to obtain the correction terms of a Hamiltonian, in the Fer expansion only an evaluation of nested commutators is required. The calculation of the infinite number of commutators, 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. Furthermore, a recent comparison among Magnus, Floquet, and Fer expansion schemes made by Takegoshi et al. [117] expressed that the Fer expansion will be more appropriated to explain experiments making use of higher-order terms. The Fer expansion can also be used as numerical method for solving Eq. (1). To obtain \( Y(t) \) from \( Y_0 \), one follows a time-stepping advance procedure. For sake of simplicity (but without loss of generality), the following constant time step is considered,

\[ h = \frac{t}{N} \], \quad \text{with} \quad t_j = jh \quad \text{and} \quad j = 0,1,2,...,N \]  

(38)

and next the approximations \( Y_j \) are computed to the exact values \( Y(t_j) \). \( Y_j \) are obtained by applying the Fer expansion in each subinterval \( [t_{j-1}, t_j] \), \( (j = 1,2,...,N) \) to the initial condition \( Y_{j-1} \). The process involves three steps. First, the expansions are truncated according to the order in \( h \) want we wish to achieve. Second, the multivariate integrals in the truncated expansions are replaced by conveniently chosen approximations. Third, the exponentials of the matrices have to be computed. Following these steps, the first order in the Fer expansion,
\[
\exp(A^{(0)}(\hat{h})) = \exp(hA(t_n + \frac{\hat{h}}{2}))y_n
\]

(39)

However, the concept of an effective Hamiltonian is not directly valid in the Fer expansion. More work is required to ascertain the feasibility of the Fer expansion in handling cases involving non-periodic and non-cyclic cases.

**III.1.3. Applications**

### III.1.3.1. Block-Siegert Shift

Following the arguments given by Haeberlen detailed in the literature \([31,87]\), the unrotated rotating frame Hamiltonian during an on-resonance RF irradiation with\

\[
H_{RF} = -2\omega_I I_x \cos(\omega t + \phi)
\]

is given by\

\[
H = H_{RF}^n = -\Delta\omega\omega_I t -\omega_I [I_x \cos(\phi) + I_y \sin(\phi)]\omega_I t (\cos(2\omega_I t - \phi) + I_z \sin(2\omega_I t - \phi))
\]

(40)

where \(\omega_I\) is the Larmor frequency of the I spins. \(\Delta\omega\) is the off-resonance value, and \(\omega_I\) is the RF nutation frequency. The period of \(H_{RF}^{on}\) (t) is \(\tau_C = \frac{\pi}{\omega_I}\). A direct integration of Eq. (40) gives

\[
F(t) = \int_0^t \! H dt = -\Delta\omega\omega_I t -\omega_I [I_x \cos(\phi) - I_y \sin(\phi)]
\]

(41)

Following Eq. (35), we obtain the following expression for \(H_{RF}^{(0)}\)

(42)

The first commutator of the above Eq. (43) is

\[
\frac{1}{2}[H, F]\.
\]

The calculated coefficient term of \((-I_x)\) is found to be the well documented Bloch-Siegert shift given by

\[
\omega_I \left(\frac{\omega_I}{2\omega_I}\right)^2
\]

(44)

### III.1.3.2. Heteronuclear dipolar decoupling

Following the work of Haeberlen \([31]\) and Ernst \([87]\), we write the Hamiltonian in the doubly rotating frame of the spin as

\[
H(t) = d_{IS} S Z (I_x \cos(\omega_I t - I_y \sin(\omega_I t)) - \Delta\omega(I_x \sin(\omega_I t - I_y \cos(\omega_I t))
\]

(45)

where \(d_{IS}\) is the dipolar coupling constant. \(\Delta\omega\) is the off-resonance value, and \(\omega_I\) is the nutation frequency of the RF irradiation on the I spins. \(H(t)\) is periodic with period \(\tau_C = \frac{2\pi}{\omega_I}\).

A direct integration of Eq. (40) gives

\[
F(t) = \int_0^t \! H dt = \frac{1}{\omega_I} d_{IS} S Z (I_x \sin(\omega_I t + I_y \cos(\omega_I t))
\]

(46)

Using the above expression Eq. (46) for \(F(t)\), and evaluating the first commutator with the relation

\[
\frac{1}{2}[H, F]\.
\]

(47)

Under off-resonance conditions, Madhu et al. \([62]\) and Haeberlen \([31]\):\

\[
H_{RF}^{(1)} \approx \frac{1}{2\omega_I} d_{IS}^2 S Z^2 I_x + \frac{1}{6\omega_I^2} d_{IS}^3 S Z^3 I_x
\]

(48)

The second term on the right-hand side in the above equation is obtained within the first-order correction in the case of Fer expansion, while in the case of AHT, this term corresponds to the second-order correction term.

### III.1.3.3. Study of interactions in solid-state NMR when irradiated with the magic echo pulse sequence

Recently, we and others used the Fer expansion approach to study interactions in solid-state NMR when irradiated with the magic-echo sequence \([33,34,99]\). The following results were obtained for the chemical shift, dipolar and quadrupolar interactions, respectively.

\[
F(t) = \frac{\Delta\omega}{\omega_I} I_x (\cos(\omega_I t - l) + \Delta\omega I_x \sin(\omega_I t - l) + \Delta\omega I_x \sin(\omega_I t - l))
\]

(49)

The first commutator of the above Eq. (43) is

\[
\frac{1}{2}[H, F](t)\.
\]

The calculated coefficient term of \((-I_x)\) is found to be the well documented Bloch-Siegert shift given by

\[
\omega_I \left(\frac{\omega_I}{2\omega_I}\right)^2
\]

(50)

where
We processed further by calculating $H^{(1)}_F$ using the value of $F_i(t)$. We have the first two orders:

$$H^{(1)}_F = -\frac{1}{2}[F_i, H^0_F] + \frac{1}{3}[F_i, [F_i, H^0_F]]$$

This can also be written as

$$H^{(1)}_F = -\frac{1}{2}[F_i, H^0_F] + \frac{1}{3}F_i \{[F_i, H^0_F]\}$$

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

### III.2. Floquet-Magnus expansion

Very recently, Mananga and Charpentier introduced the Floquet-Magnus expansion approach to solid state NMR and spin physics [18,115]. This approach is unique in spin physics and useful to shed new lights on AHT and FLT [18-28,44,72-93]. The Floquet-Magnus expansion is a new theoretical tool for describing spin dynamics in solid-state NMR. This approach (FME) is an extension of the popular Magnus Expansion and Average Hamiltonian Theory. Calculations could be performed in a finite-dimensional Hilbert space instead of an infinite dimensional space within the Floquet theory. This approach controls the spin dynamics in solid state NMR and makes use of its unique solution that has the required structure and evolves in the desired Lie group. All three theoretical approaches (AHT, FLT, and FME) are equivalent in the first order which corresponds to the popular average Hamiltonian.

$$H^{(0)}_{\text{AHT}} = H_{\text{eff(FLT)}} = H^{(FMB)}_F = H_0$$

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. The approach of FME is essentially distinguished from other theories with its famous function $\Lambda_n(t)$ which provides an easy and alternative way for evaluating the spin behavior in between the stroboscopic observation points. Considering the solution of the Eq. (1) in the form of the exponential form, and the function $\mathcal{Q}(t)$ representing the argument of the exponential solution ($e^{\mathcal{Q}(t)}$), the relationship with the regular Magnus expansion can be obtained from [18]

$$\frac{\mathcal{Q}(T)}{T} = e^{-\Lambda(0)} Fe^{\Lambda(0)}$$

The Eq. (2) points out that it is only in the case $\Lambda(0) = 0$

(57)

that the FME gives the AHT as provided by the ME. The Eq. (2) is the general approach of AHT called FME which gives also the option of $\Lambda(0) \neq 0$. The function $\Lambda_n(t)$ is connected to the appearance of features like spinning sidebands in MAS. The FME general formula are given by [18]

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

with

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

where $n = 1,2,3,...$ and

$$G_n(\tau) = H(\tau)$$

The $\Lambda_n(t)$ functions ($n = 1,2,3,...$) 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 of NMR, this function can be used to quantify the level of productivity of double quantum terms.

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 [45]. Like the FLT, the FME describes the time evolution of the spin system at all times. The FME is more useful in simplifying calculations and providing more intuitive understanding of spin dynamics processes. In the articles by Mananga and Charpentier [18,115], we showed that the lowest-order term $F_1$ as provided by AHT, FLT, and FME are all identical. Next, using the FME, we calculated for each interaction, the first order function ($\Lambda_1(t)$) that provide 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. The same article by Mananga et al. [18] showed 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.

### III.2.1. Useful equations

Considering the initial conditions to be $\Lambda(0) = 0$ (i.e., $P(0) = I$ ), Blanes et al. [44,66,72] derived explicitly, the following equations:

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

(63)
\[ F_1 = \frac{1}{T} \int_0^T H(x) \, dx \]  

(64)

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

(65)

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

(66)

\[ \Lambda_n(t) = \frac{i}{T} \int_0^T \left[ \Lambda_n, H + F_1 \right] \, dx - \frac{1}{12T} \int_0^T \left[ \Lambda_n, \left[ \Lambda_n, H - F_1 \right] \right] \, dx - tF_n \]  

(67)

The above equations are now considered to be a particular case (\( \Lambda(0) = 0 \)) of a more general representation of the FME with \( \Lambda(0) \neq 0 \). The general formula for the contribution of the FME is given as follows [18]:

\[ \Lambda_n(t) = \Lambda_n(0) + \frac{i}{T} \int_0^T G_n(x) \, dx - tF_n \]  

(69)

with

\[ F_n = \frac{1}{T} \int_0^T G_n(x) \, dx \]  

(70)

The first order contributions to the FME give explicitly

\[ G_1(x) = H(x) \]  

(71)

\[ G_2(x) = -\frac{i}{2} \left[ H(x) + F_1, \Lambda_1(x) \right] \]  

(72)

\[ G_n(x) = -\frac{i}{2} \left[ H(x) + F_1, \Lambda_1(x) \right] - \frac{i}{2} \left[ F_1, \Lambda_n(x) \right] - \frac{1}{12} \left[ \Lambda_n(x), \left[ \Lambda_n(x), H(x) - F_1 \right] \right] \]  

(73)

Symbolic calculation software can enable formal derivation of higher order terms. In the above equations (Eqs. (11-21)), the \( \Lambda_n(t) \) functions with \( n = 1, 2, 3, \ldots \), 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 \( F \). This function (\( \Lambda_n(t) \)) can be useful to quantify the level of productivity of double quantum terms such as in the article [66,67].

### III.2.2. Advantages and limitations

The aims of the FME is to bridge the AHT to the Floquet Theorem but in a more concise and efficient formalism [18]. Calculations can then be performed in a finite-dimensional Hilbert space instead of an infinite dimensional space within the Floquet theory. We expected that the FME will provide means to more accurately and efficiently perform spin dynamics simulation and for devising new RF pulse sequence. The FME provides a quick means to calculate higher order term allowing the disentanglement of the stroboscopic observation \( \Lambda(t) \) and effective Hamiltonian \( F \) that will be useful to describe spin dynamics at all times in solid-state NMR and understand different synchronized or non-synchronized experiments.

The FME offers a simple way to handle multiple incommensurate frequencies and thus open perspectives to deal with multi-mode Hamiltonian in the Hilbert space. This approach can provide new aspects not present in AHT and FT such as recursive expansion scheme in Hilbert space that can facilitate the development of new or improvement of existing pulse sequence. The FME approach is essentially distinguished from the operator-based Floquet theory with its function \( \Lambda(t) \) which provides an easy and alternative way for evaluating the spin behavior in between the stroboscopic observation points. In the Floquet-Magnus approach, even when the first and second order \( F_1 \) and \( F_2 \) of the effective Hamiltonian are identical to their counterparts in AHT, FT, and operator-based Floquet theory, the \( \Lambda(t) \) functions provide an easy 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. The effective Hamiltonians of the FME [18] and the operator-based Floquet theory [38,39] seem to be the closest one compared to the other approaches.

### III.2.3. Applications

#### III.2.3.1. Simple cases

**Common form of Hamiltonian in solid-state NMR**

Here, we revisited the static perturbation theory [18,68,101] which has been shown to yield the correct form of Zeeman truncated NMR interactions without the limit of stroboscopic observation of the AHT. This gave us the opportunity to shed light on the FME scheme and the derivation of a criterion for the two theories being compatible.

For the sake of simplicity (but without loss of generality), we considered the Hamiltonian

\[ H = \omega_0 I_2 + \lambda \sum_m (-1)^m R_{2,-m} T_{2,m} \]  

(74)

This is a common form of Hamiltonian in solid-state NMR. \( \omega_0 I_2 \) is the Zeeman interaction, \( R_{2,m} \) are the lattice parts of the internal interaction which encode its orientational dependence with respect to the magnetic field, \( T_{2,m} \) are second rank m-order spherical tensor describing the spin system as defined by \( [I_2, T_{2,m}] = mT_{2,m} \).

The static perturbation theory (SPT) in terms of the irreducible tensor operators gives the diagonal Hamiltonian (with respect to \( \omega_0 I_2 \))

\[ H_{SPT} = \omega_0 I_2 + \lambda R_{2,0} T_{2,0} + \frac{\lambda^2}{2\omega_0} \sum_{m \neq 0} \frac{R_{2,m} R_{2,-m}}{m} [T_{2,m}, T_{2,-m}] \]  

(75)

As discussed in the seminal work [68], discrepancies between AHT and FT appear in the rotating frame representation (or more generally in the interaction frame) where the Hamiltonian becomes time-dependent:

\[ \tilde{H}(t) = e^{i\omega_0 t I_2} H e^{-i\omega_0 t I_2} = \lambda \sum_m (-1)^m R_{2,-m} T_{2,m} e^{i\omega_0 m} \]  

(76)

The FME expansion Eqs. (63) and (64) yields as first order terms:

\[ F_1 = \lambda R_{2,0} T_{2,0} \]  

(77)
\[ \Lambda_1(t) = \frac{\alpha}{\omega_0} \sum_{m=0}^{\infty} \frac{R_{2,m}T_{2,m}}{m \omega_0} e^{im\alpha t} \]

(78)

whereas the AHT (stroboscopic detection) yields [18]

\[ \Lambda_1(t) = \frac{\alpha}{\omega_0} \sum_{m=0}^{\infty} \frac{R_{2,m}T_{2,m}}{m \omega_0} (e^{im\alpha t} - 1) \]

(79)

Also, the FME scheme [18] provides the same second order term as in SPT theory

\[ F_2 = \frac{\alpha^2}{2 \omega_0} \sum_{m=0}^{\infty} \frac{R_{2,m}R_{2,-m}}{m} \left[ T_{2,m}, T_{2,-m} \right] \]

(80)

This shows that FME provides an expansion in the rotating frame which is in agreement with the static perturbation theory and Van Vleck transformations. This is not the case of the Magnus expansion. This agreement can be easily explained by the connection that exists between the FME and SPT propagators as explained in the original article [18].

Extension to multimode Hamiltonian

The application of FME to multimode Hamiltonian with frequencies \( \omega = (\omega_1, ..., \omega_N) \) is straightforward. Considering the generalized Fourier expansion of the Hamiltonian \( (\omega = (\omega_1, ..., \omega_N) \) represented by the frequency indices)

\[ H(t) = \sum_i H_{li} \exp(-i m \omega_i t) \]

(81)

we obtain

\[ \Lambda_1(t) = \sum_{m,\omega} \frac{H_{li}}{i m \omega} e^{-i m \omega t} \]

(82)

and

\[ F_1 = \sum_{m,\omega} H_{li} \]

(83)

Similarly, calculation of second order terms is straightforward [18]. These expressions highlight the fact that the multimode Hamiltonian case can be easily treated in Hilbert space with the FME.

III.2.3.2. Study of interactions in solid-state NMR when irradiated with the magic echo pulse sequence

Here, the use of FME is 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 [65].

For Chemical Shift (CS):

\[ F_{\text{CS}}(t) = \frac{1}{\Delta \omega} \left( \frac{1}{2} (1 - \cos \omega_0 (2\tau - \alpha)) - \frac{1}{\Delta \omega} \right) \sin \omega_0 (2\tau - \alpha) - \frac{1}{\Delta \omega} \alpha \]

(84)

\[ \Lambda_{\text{CS}}(t) = \frac{1}{\Delta \omega} \left( \frac{1}{2} (1 - \cos \omega_0 (2\tau - \alpha)) - \frac{1}{\Delta \omega} \right) \sin \omega_0 (2\tau - \alpha) - \frac{1}{\Delta \omega} \alpha \]

\[ \sum_{m=0}^{\infty} \frac{2}{m \omega_0} \left[ (e^{m \omega_0 \alpha} - 1) \right] F_{\text{CS}}(t) \]

(85)

where \( I_A, I_B, I_C, \) and \( I_D \) are given by:

\[ I_A = \int e^{i \omega_0 \alpha} \cos(\omega_0 \alpha \tau) d\tau = \frac{1}{2 \omega_0 \alpha} \left( \frac{\omega_0 \alpha}{2 \omega_0 \alpha - 4 \omega_0 \alpha} \right) \sin(\omega_0 \alpha \tau) + 4 \cos(\omega_0 \alpha \tau) \cos(\omega_0 \alpha \tau) + 4 \cos(\omega_0 \alpha \tau) \sin(\omega_0 \alpha \tau) \]

(94)

\[ I_B = \int e^{i \omega_0 \alpha} \sin(\omega_0 \alpha \tau) d\tau = \frac{1}{2 \omega_0 \alpha} \left( \frac{\omega_0 \alpha}{2 \omega_0 \alpha - 4 \omega_0 \alpha} \right) \sin(\omega_0 \alpha \tau) + 4 \cos(\omega_0 \alpha \tau) \cos(\omega_0 \alpha \tau) + 4 \cos(\omega_0 \alpha \tau) \sin(\omega_0 \alpha \tau) \]

(95)

\[ I_C = \int e^{i \omega_0 \alpha} \sin(\omega_0 \alpha \tau) d\tau = \frac{1}{2 \omega_0 \alpha} \left( \frac{\omega_0 \alpha}{2 \omega_0 \alpha - 4 \omega_0 \alpha} \right) \sin(\omega_0 \alpha \tau) + 4 \cos(\omega_0 \alpha \tau) \cos(\omega_0 \alpha \tau) + 4 \cos(\omega_0 \alpha \tau) \sin(\omega_0 \alpha \tau) \]

(96)

\[ I_D = \int e^{i \omega_0 \alpha} \sin^2(\omega_0 \alpha \tau) d\tau = \frac{1}{2 \omega_0 \alpha} \left( \frac{\omega_0 \alpha}{2 \omega_0 \alpha - 4 \omega_0 \alpha} \right) \sin(\omega_0 \alpha \tau) + 4 \cos(\omega_0 \alpha \tau) \cos(\omega_0 \alpha \tau) + 4 \cos(\omega_0 \alpha \tau) \sin(\omega_0 \alpha \tau) \]

(97)
\[ I_j = \left[ e^{-i\omega_0 t} \sin(2\omega_0 t') dt' \right] \frac{1}{2} \left[ \cos(\omega_0 t) + 2\omega_0 \exp(-i\omega_0 t) \right] + i\omega_0 \exp(-i\omega_0 t)\sin(2\omega_0 t) \] (98)

\[ I_j = \left[ e^{-i\omega_0 t} \sin(2\omega_0 t') dt' \right] \frac{1}{2} \left[ \cos(\omega_0 t) - 4\omega_0 \exp(-i\omega_0 t) \right] - 2i\omega_0 \sin(\omega_0 t') \exp(-i\omega_0 t) \cos(2\omega_0 t) + + i\omega_0 \exp(-i\omega_0 t)\sin(2\omega_0 t) \] (99)

For Quadrupolar interaction (Q):

Using Fig. 3 for magic echo pulse sequence, we have:

\[ F_{\text{qep}} = \frac{1}{\tau} \frac{12\alpha}{\pi} l_{\sin} + \frac{4(3\alpha - \tau)\omega_0}{7\tau} [I_{\sin}, I_{\sin} + I_{\sin}, I_{\sin} - 2I_{\sin}, I_{\sin}] \] (100)

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

Fig. 5: The relation \( 1 - \theta(t) \) is only valid during the interval where \( \theta(t) \) acts.

In this scheme, we have the following relation in each part:

\[ a_k^{(1)} = \frac{1}{\tau_R} \int_0^{\tau - 2\alpha} e^{i\phi \alpha t} dt' \] (101)

\[ a_0^{(1)} = \frac{\tau - 2\alpha}{\tau_R} \] (102)

\[ a_k^{(1)} = \frac{1}{ik2\pi} e^{i\phi \alpha (\tau - 2\alpha)} - 1 \] (103)

\[ a_k^{(2)} = \frac{1}{\tau_R} \left[ \int_0^{\tau - \alpha} e^{i\phi \alpha t'} dt' + \int_{6\tau + \alpha}^{7\tau} e^{i\phi \alpha t'} dt' \right] \] (104)

\[ a_0^{(2)} = \frac{1}{\tau_R} (2\tau - 2\alpha) \] (105)

\[ a_k^{(2)} = \frac{1}{ik2\pi} \left[ e^{i\phi \alpha (2\tau - \alpha) - e^{i\phi \alpha \tau} + e^{i\phi \alpha 7\tau} - e^{i\phi \alpha (6\tau + \alpha)} \right] \] (106)

However, for mathematical convenience, we made the following approximation: we neglected the first free evolution time, and considered the free evolution time given in figure 6:

\[ a_k^{(1)} = \frac{1}{\tau_R} \int_0^{\tau - 2\alpha} e^{i\phi \alpha t} dt \] (108)

\[ a_k^{(2)} = \frac{1}{\tau_R} \int_0^{5\tau + 2\alpha} e^{i\phi \alpha t} dt \] (109)

From the above equations, we obtain the following criteria

\[ a_0 = c - \phi \] (110)

\[ a_k^{(2)} = a_k^{(1)} e^{i2\pi(5\tau + \phi)} = \frac{1}{2\pi ik} \left[ e^{i2\pi(\phi + \epsilon)} e^{i2\pi\epsilon} \right] \] (111)

with

\[ \phi = \frac{\alpha}{\tau_R} \] (112)

\[ \tau = c\tau_R \] (113)

The first order of the FME is computed to be:

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

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

\[ \tilde{H}(t) = \tilde{H}(t) + \tilde{H}(t) + \tilde{H}(t) + \tilde{H}(t) + \tilde{H}(t) + \tilde{H}(t) + \tilde{H}(t) \] (107)

where \( \tilde{H}(t) \), \( \tilde{H}(t) \), \( \tilde{H}(t) \), \( \tilde{H}(t) \), \( \tilde{H}(t) \), \( \tilde{H}(t) \), \( \tilde{H}(t) \), \( \tilde{H}(t) \), \( \tilde{H}(t) \), \( \tilde{H}(t) \), \( \tilde{H}(t) \), \( \tilde{H}(t) \), and \( \tilde{H}(t) \) correspond to the toggling Hamiltonian for the intervals \( \delta_2 \), \( \delta_3 \), \( \delta_4 \), \( \delta_5 \), \( \delta_6 \), \( \delta_7 \), \( \delta_8 \), respectively, given in the article [64,65].

Processing as previously, the first and second part of the sequence are:

\[ a_k^{(1)} = \frac{1}{\tau_R} \int_0^{\tau - 2\alpha} e^{i\phi \alpha t} dt \] (108)

\[ a_k^{(2)} = \frac{1}{\tau_R} \int_0^{5\tau + 2\alpha} e^{i\phi \alpha t} dt \] (109)

From the above equations, we obtain the following criteria

\[ a_0 = c - \phi \] (110)

\[ a_k^{(2)} = a_k^{(1)} e^{i2\pi(5\tau + \phi)} = \frac{1}{2\pi ik} \left[ e^{i2\pi(\phi + \epsilon)} e^{i2\pi\epsilon} \right] \] (111)

with

\[ \phi = \frac{\alpha}{\tau_R} \] (112)

\[ \tau = c\tau_R \] (113)
Considering Fig. 6, we remark that the magic echo pulse sequence remove the \( \theta(t) \) dependence and calculation of \( F_1 \) and \( \Lambda_1(t) \) become less lengthy.

### III.2.3.3 Investigation of the Effect of Finite Pulse Errors on BABA Pulse Sequence

![BABA pulse sequence](image1)

![BABA pulse sequence with finite pulse width](image2)

In Fig. 8, the relation \( \Theta(t) = 1 - \Theta(t) \) is valid only during the interval where \( \theta(t) \) acted.

We studied the finite pulse widths effects for the BABA pulse sequence using the Floquet-Magnus expansion approach \[67,102\]. We investigated the case \( \theta = \pi \) and considered a system of 2 spins. Only DQ terms are considered for the function \( \Lambda_1(t) \). We considered the simple case where the rotations are: \( \alpha = \beta = \gamma = 0 \).

The coefficient \( C_n^j \) are

\[
C_1 = -\frac{1}{\sqrt{3}} \sin(\theta) \cos(\theta)e^{-i\phi},
C_{-1} = 0, \quad C_2 = \frac{1}{(2\sqrt{6})\sin^2(\theta)e^{-2i\phi}}, \quad C_{-2} = 0.
\]

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 function \( \Lambda_1(t) \) is written as:

\[
\Lambda_1(t) = \frac{3}{2\sqrt{6}} b_j \left[ a_1 C_1 \left( \frac{\tau + 4\tau}{2} \right) \psi + a_2 C_2 \left( \frac{\tau + 4\tau}{2} \right) \psi \right] (I_{11} - I_{22})
\]

(115)

where

\[
\psi = \frac{t}{\tau_R},
\]

(116)

\[
\phi = \frac{2\pi}{\tau_R},
\]

(117)

\[
a_1 = -\frac{1}{2\pi} e^{-ij(1+\phi)} \left[ e^{-i\pi(1-2\phi)} - 1 \right].
\]

(118)

and

\[
a_2 = -\frac{1}{4\pi} e^{-ij(1+\phi)} \left[ e^{-i2\pi(1-2\phi)} - 1 \right].
\]

(119)

which lead to

\[
\frac{\Lambda_1(\psi, \phi)}{b_j \tau_R} = \frac{3}{2\sqrt{6}} \left( -a_1 + \frac{1}{2\sqrt{2}} a_2 \right) (1 + \phi) \psi (I_{11} - I_{22})
\]

(120)

As reported in the reference \[67\], we considered the case, \( 0.1 \leq \phi \leq 0.606 \), which corresponds to the spinning frequencies \( \frac{\Omega_R}{2\pi} = 5 - 10 \) kHz, and to the recoupling RF fields \( \frac{\Omega_{RF}}{2\pi} = 25 - 50 \) kHz. We generated two types of plots from the Eq. (120). First, the plot of \( \frac{\Lambda_1(t)}{b_j \tau_R} \) versus \( \psi = \frac{t}{\tau_R} \), while keeping \( \phi = \frac{2\pi}{\tau_R} \) constant corresponding to the Fig. 9. The plot of \( \frac{\Lambda_1(t)}{b_j \tau_R} \) versus \( \psi = \frac{2\pi}{\tau_R} \), while keeping the time \( t \) constant corresponding to Fig. 10.
Fig. 10: Numerical Functions of Finite Pulse BABA Sequence with $\Lambda_1(t)$ versus $\phi = \frac{2 \tau_p}{\tau_R}$, for $\phi = 0.1$ and $\phi = 0.606$. The size of $\Lambda_1(t)$ determines the amplitude of the DQ coherence, which indicates the degree of efficiency of the scheme. A closer look at Fig. 9 and 10 (BABA with finite pulse widths) compared BABA with delta-pulse sequences [66] shows that the magnitude of the DQ terms of BABA with finite pulses is small compared to the magnitude of BABA with $\delta$-pulse sequences, as expected. Fig. 10 a) shows the plot of the function $\Lambda_1(t)$ for BABA pulse sequence with finite pulse widths versus the dimensionless number $\phi = \frac{2 \tau_p}{\tau_R}$, for $t = 1$ ms. Fig. 10 b) shows the plot of the same function $\Lambda_1(t)$ versus $\phi = \frac{2 \tau_p}{\tau_R}$ for the two cases: $t = 1$ ms and $t = 2$ ms. As with Fig. 9, due to the complexity of the function $\Lambda_1(t)$, real, imaginary, and absolute parts are plotted separately as function of $\phi$. In Fig. 10 b), the symbols “square”, “plus”, and “hexagram” represent respectively the real, imaginary, and absolute parts of the function $\Lambda_1(t)$ for $\phi = 0.606$. 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 with finite widths. The plot can be considered as a quantitative representation of the amplitude of the DQ coherence as a function of $\phi$. The size of $\Lambda_1(t)$ determines the amplitude of the DQ coherence, which indicates the degree of efficiency of the scheme. A closer look at Fig. 9 and 10 (BABA with finite pulse widths) compared BABA with delta-pulse sequences [66] shows that the magnitude of the DQ terms of BABA with finite pulses is small compared to the magnitude of BABA with $\delta$-pulse sequences, as expected. Fig. 10 a) shows the plot of the function $\Lambda_1(t)$ for BABA pulse sequence with finite pulse widths versus the dimensionless number $\phi = \frac{2 \tau_p}{\tau_R}$, for $t = 1$ ms. Fig. 10 b) shows the plot of the same function $\Lambda_1(t)$ versus $\phi = \frac{2 \tau_p}{\tau_R}$ for the two cases: $t = 1$ ms and $t = 2$ ms. As with Fig. 9, due to the complexity of the function $\Lambda_1(t)$, real, imaginary, and absolute parts are plotted separately as function of $\phi$. In Fig. 10 b), the symbols “square”, “plus”, and “hexagram” represent respectively the real, imaginary, and absolute parts of the function $\Lambda_1(t)$ for $\phi = 0.606$. These functions depend on the DQ terms. It can easily be seen that, when $\phi = \frac{2 \tau_p}{\tau_R}$ increases, the magnitude of the double quantum terms decreases, as expected. When $\phi \to 0$, the magnitude of the DQ term maximum corresponding to the delta-pulse sequence. However, when $\phi = 0.5$ corresponding to $\tau_p = \frac{\tau_R}{4}$, we have $\Lambda_1(t) = 0$. The strength of the DQ terms decreases, cancel and build up again. This dynamic predicts that a full decoupling is
possible, which occurs at $\phi = 0.5$. The plot of the magnitude of the double quantum term of $A_i(t)$ as a function of the pulse length gives a basic understanding of the experiment such as how to select robust finite pulse widths and how to select finite pulse widths that maximize or minimize double quantum terms. The study of this function could be helpful in predicting the conditions of decoupling.

IV. Discussion

IV.1. Propagators

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:

$$U(t) = \exp\left(-i\bar{H}(t)\right)$$

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:

$$U(t) = P(t) \exp\left(-iH_F t\right)$$

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,

$$P(0) = P(nt_c) = 1$$

and by assuming stroboscopic observation which shows the identity

$$H_F = \bar{H}$$

The FME propagator is given by:

$$U(t) = P(t) \exp\left(-iH_F t\right) P^\dagger(0)$$

Here the constraint of stroboscopic observation is removed.

$$P(t) = \exp\left\{-i\Lambda(t)\right\}$$

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

$$U(t) = \prod_{k=1}^{\infty} \exp\left[H_{F_k}(t)\right] = \exp\left[H_{F_1}(t)\right] \exp\left[H_{F_2}(t)\right] \cdots$$

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

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

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. The Fer and Magnus proposals endeavor to complement the general solution

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

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.

IV.2. Convergences

The convergence of the Magnus expansion (AHT), Floquet theory, Floquet-Magnus expansion, and Fer expansion are extensively discussed in the literature [18,22,44,63,71-97,104-106]. In general, the Magnus series does not converge unless $H(t)$ is small in a suitable sense as discussed published articles [105-107]. The discussion of the convergence of the Floquet theory was presented by Maricq [105,106] and elsewhere [18]. Matti Maricq used an indirect method that took advantage of the periodicity of $P(t)$ and the method of Picard approximations to produce a convergent sequence for the propagator $U(t)$. Because the Floquet scheme is a convergent sequence, once the convergence is fulfilled in one period, it is assured for any value of time. On the contrary, in the general Magnus case, the bound always gives a running condition. Blanes et al. [44,73] and Casas et al. [72,75] showed that absolute convergence of the Floquet-Magnus series is guaranteed at least if

$$\int_0^T \|H(t)\|dt < r_C (FME) = 0.20925$$

The convergence of Fer expansion is much faster than that of Magnus expansion and is well defined by Blanes et al. [62,74,88].

V. Conclusion

We have attempted to present 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. We also present two developing and emerging theories in solid-state NMR (FME, FE). The combinations of two or more of the theories described within will provide a framework for treating time-dependent Hamiltonian in NMR in a way that can be easily extended to both synchronized and several non-synchronized 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 experiments. The intention of writing this historical overview of the two major theories in NMR and the developing theories 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 specialists. We did not discuss the effective Hamiltonian of these theories in this review article. However, this will be the subject of our forthcoming article.

An extremely important point, which is currently been developed, to tackle is the possibility of enhancing 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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VI. REFERENCES


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