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Theoretical approaches to control spin dynamics in solid-state nuclear magnetic resonance

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Abstract. This article reviews theoretical approaches for controlling spin dynamics in solid-state nuclear magnetic resonance. We present fundamental theories in the history of NMR, namely, the average Hamiltonian and Floquet theories. We also discuss emerging theories such as the Fer and Floquet-Magnus expansions. These theories allow one to solve the time-dependent Schrodinger equation, which is still the central problem in spin dynamics of solid-state NMR. Examples from the literature that highlight several applications of these theories are presented, and particular attention is paid to numerical integrators and propagator operators. The problem of time propagation calculated with Chebychev expansion and the future development of numerical directions with the Cayley transformation are considered. The bibliography includes 190 references.

Keywords. Average Hamiltonian theory; Floquet theory; Fer expansion; Floquet-Magnus expansion; Chebyshev expansion; Cayley method.

1. Introduction

The time-dependent Schrodinger equation is one of the main frameworks unifying the quantum mechanical, atomic and molecular physics descriptions of matter.[1–5] This framework is particularly unique, permitting a consistent treatment of the spin dynamics in nuclear magnetic resonance (NMR). Such spin dynamics are central in the description of the quantum measurement process leading to the NMR signal and also in designing sophisticated pulse sequences and understanding of different experiments.[6–150]

The present review article presents some direct applications of major theories in NMR spectroscopy such as the average Hamiltonian theory (AHT),[19,44] the Floquet theory (FLT),[20–23] the Fer expansion (FE)[62,63] and the Floquet-Magnus expansion (FME).[18,44] Methodologies of these theoretical approaches based on numerical integrators and their propagator operators are reviewed.[44] Examples from literature highlighting some applications of these theoretical schemes are also given.[151,152] We mainly treat the problems of Bloch-Siegert shift, continuous waves (CWs) decoupling and interactions in solid-state NMR when irradiated with magic echo pulse sequence with all the theories (AHT, FLT, FE and FME) to give the reader the possibility of appreciating the advantages and limitations of these theories and approaches. Our analysis is mainly based on effective Hamiltonians. Effective Hamiltonians are necessary to understand how the pulse sequences work. We used the time-dependent Hamiltonians to derive effective Hamitonians useful to compare the similarities and contrasts of the theories therein. During different times of the experiment, different effective Hamiltonians are expected. All pulse sequences use rf irradiation schemes that lead to time-dependent Hamiltonians for decoupling or recoupling purposes. Furthermore, different rf irradiation schemes in combination with magic-angle spinning (MAS) lead to different types of effective Hamiltonians.[189] With the increase of the level of sophistication of NMR experiments, higher-order terms are of increasing importance, such as in diffusion experiments, or like triple-resonance CWs radio frequency irradiation under magic-angle spinning (MAS). Therefore, it is important to consider also theories such as Fer and Floquet-Magnus expansions that allow the calculation of higher-order terms more easily. In this review, we do not present unpublished solutions or unsolved problems such as theoretical treatment of problems with more than four frequencies when the Floquet theory or Floquet-Magnus expansion is used.[39,66]

Without going into details, we highlight potential future NMR numerical simulations and theoretical directions such as the time evolution propagation calculated by Chebychev expansion[153–158] and the Cayley method.[159–164] This means that spin dynamics systems amenable to perturbative treatment still deserve much attention.

2. Average Hamiltonian Theory

The average Hamiltonian theory (AHT) has evolved as a powerful technique of analysis in the development of high-resolution NMR spectroscopy. The Magnus expansion[44,69–71,165–179] has been systematically used in NMR, in particular in solid-state NMR where it forms the basis of AHT. This expansion was first applied to NMR in 1968 by Evans[69] and Haeberlen and Waugh.[19] Since that time, the ME has been instrumental in the development of improved techniques in NMR spectroscopy.[70] 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.[19] This approach is the most commonly used method to treat theoretical problems in solid-state NMR and have been used sometimes abusively.[68] 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 $\overline{H}$ 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).

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.[6,18,19,26,33–36,44] 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.[79,80,89,142]

2.1 *Propagator and Magnus expansion*

2.1a *Propagator*: The central result of AHT is obtained by expressing the evolution propagator $U(t_c)$ by an average Hamiltonian $\overline{H}$ and using the Magnus expansion, which forms the basis of AHT.[19,26,34–36] The AHT propagator is given by

$$U(t_c) = \exp\left\{-i\overline{H}(t_c)t_c\right\}, \tag{1}$$

where $\overline{H}(t_c)$ is the average Hamiltonian and t_c corresponds to the period of a periodic Hamiltonian $H(t)$.

2.1b *Magnus expansion*: The Magnus expansion[44,69–85] was first applied to NMR in 1968 by Evans[69] and Haeberlen and Waugh.[19] Since that time, the ME has been instrumental in the development of improved techniques in NMR spectroscopy.[44,70] The Magnus expansion provides a solution to the initial value problem

$$\begin{aligned}\frac{dU}{dt} &= -iH(t)U(t), U(t_0)\\ &= U_0, t \in \Re, U(t) \in C^n, -iH(t) \in C^{n\times n},\end{aligned} \tag{2}$$

in terms of exponentials of combinations of the coefficient matrix $-iH(t)$. Eq. (2) is a first-order linear homogeneous system of differential equations in which $Y(t)$ is the unknown $n-$dimensional vector function. In general, U_0, U and $-iH(t)$ are complex valued. The scalar case, $n = 1$, has the general solution

$$U(t) = \exp(-\int_{t_0}^{t} iH(t')dt')U_0. \tag{3}$$

This expression is still valid for $n > 1$ if the matrix $-iH(t)$ is constant; or the commutator $[H(t_1), H(t_2)] = 0$,for any pair of values of t, $t_1$and t_2. In general, there is no compact formula for the solution of eq. (2) and the Magnus proposal endeavour to complement eq. (3) in the following direction. If a term is added to the argument in the exponential such as

$$U(t) = \exp(-\int_{t_0}^{t} iH(t')dt' + M(t, t_0))U_0, \tag{4}$$

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 $-iH(t)$ belongs to a given Lie algebra, if we express $U(t) = U_1(t, t_0)U_0$, then $U_1(t, t_0)$ belongs 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. 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.

2.2 *Applications of average Hamiltonian theory*

The method of AHT has been gradually applied to many theoretical problems in NMR and in solid-state NMR in particular.[68] For example, we used the

technique to compare the efficiency of the magic echo cycle and the simple two-pulse quadrupolar echo sequence. 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.[31,33–35,99,112,113] AHT has played a major role in NMR for developing, designing, and improving the performance of pulse sequences. For example, the technique of AHT has been very useful in designing and constructing composite pulses sequences. Composite pulses are the decomposition of a single pulse into a product of a number of constituent pulses.[135–137] These types of pulses have been developed to compensate for rf inhomogeneity, off-resonance effects, and phase distortion. Theoretical procedure for constructing composite pulses that compensate the inhomogeneities of electric field gradient and radio frequency field strength for nuclear quadrupole resonance spectroscopy uses a similar technique than AHT.[138]

The 12 chemical physics articles cited in this section describe some interesting applications of AHT in the development of pulse sequences. This include the use of AHT to calculate homonuclear dipole–dipole couplings and chemical shifts for the simple pulse sequence (delta-function) called DRAMA,[115] continuous rf irradiation with the pulse sequence called 2Q-HORROR,[116] finite-pulse recoupling sequences such as finite-pulse radio-frequency-driven recoupling (fpRFDR),[117,118] chemical-shift-driven recoupling including rotational resonance[121–128] and radio-frequency-driven-recoupling (SEDRA).[121–127] An important utility of AHT to exploit the mathematical symmetry principles in the design of NMR multiple-pulse sequences should be recongnized.[114]

2.2a *Symmetry in the design of NMR multiple-pulse sequences using AHT*: Nearly a decade and half ago, Eden and Levitt developed a set of selection rules based on the symmetry of the internal interactions and Euler angles.[103,114] Levitt's group has exploited symmetry arguments in order to simplify the design of RF pulse sequences in the presence of sample rotation.[129–132] Theorems are presented, which allow one to predict the elimination of many average Hamiltonian terms. These findings are useful to study important problems in solid-state NMR such as the heteronuclear decoupling in the presence of rapid MAS, the homonuclear recoupling interactions of the irradiated spins, higher-order multiple-quantum excitation, and selection of isotropic interactions. Indeed, several groups have developed symmetry theorems for suppressing average Hamiltonian terms in the presence of time-independent internal spin interactions, but most of these results do not apply strictly in a rotating sample.[90,97] Fortunately, Levitt and co-workers developed the *selection rules* based on general symmetry properties of pulse sequences that allow the development of recoupling and decoupling sequences as well as many other experiments. The selection rules reveal which types of interactions can be recoupled by a sequence with a given symmetry.[90–92]

2.2b *Bloch–Siegert shift*: The Hamiltonian for the Bloch–Siegert shift for single spin-1/2 under on-resonance rf irradiation on the I spin may be written as[62]

$$\mathrm{H}_{Lab}(t) = 2\omega_1 \cos(\omega_{RF} t) I_X + \omega_0 I_Z \tag{5}$$

The above relevant Hamiltonian in the interaction frame defined by the operator

$$U_{RF}(t) = e^{-i\omega_{RF} I_Z t}, \tag{6}$$

that is,

$$\begin{aligned} \tilde{H}_{Rot}(t) &= e^{-i\omega_{RF} I_Z t} H_{Lab}(t) e^{i\omega_{RF} I_Z t} \\ &= (\omega_0 - \omega_{RF}) I_Z + \omega_1 I_X + \omega_1 \cos(2\omega_{RF} t) I_X \\ &\quad + \omega_1 \sin(2\omega_{RF} t) I_Y \end{aligned} \tag{7}$$

The first-order AHT expansion is the result of resonance offset and rf irradiation,

$$\overline{\mathrm{H}}^{(1)} = \frac{1}{\tau_C} \int_0^{\tau_C} dt \tilde{H}_{Rot}(t) = (\omega_0 - \omega_1) I_Z + \omega_1 I_X \tag{8}$$

and the second-order AHT expansion is the well-documented Bloch–Siegert shift

$$\overline{\mathrm{H}}^{(2)} = \frac{-i}{2\tau_C} \int_0^{\tau} dt_2 \int_0^{t_2} dt_1 \left[\tilde{H}(t_2), \tilde{H}(t_1) \right] = \omega_{RF} \left(\frac{\omega_1}{2\omega_{RF}} \right)^2 I_Z \tag{9}$$

These shifts are significant for homonuclear and heteronuclear decoupling if the irradiation frequency is close to the detection frequency.

2.2c *Interactions in solid-state NMR when irradiated with solid echo and magic echo pulse sequences*: The interactions of spin systems in NMR have been extensively described by Levitt,[75] Veshtort and Griffin,[76] and Bak *et al.*[77] In this part of the review paper, we summarized the various forms of Hamiltonians subject to the secular approximation of high-field truncation. The Hamiltonian of the spin system is the sum of the different physical influences or interactions acting on the nuclear spin such as the chemical shift, dipole–dipole coupling, or quadrupolar coupling.

Mathematically, the spin Hamiltonian in NMR can be written as

$$\mathrm{H} = \sum_{\Lambda} \mathrm{H}^{\Lambda}, \tag{10}$$

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

In high-magnetic-field NMR, all interaction terms have the spin quantum numbers equal to zero ($\mu = 0$, $m = 0$), and the spin Hamiltonians are truncated by the secular approximation. NMR interactions are written explicitly by the following expressions[31]

$$H_{RF} = \sum_{i} \left|\omega^{i}_{RF}(t)\right| (I_{ix}\cos\phi_i + I_{iy}\sin\phi_i), \tag{11}$$

$$H_{CS} = \sum_{i} \omega^{i}_{CS,0}(t) I_{iz}, \tag{12}$$

$$H_J = \sum_{ij} -\omega^{ij}_{J_{iso,0}}(t)\frac{1}{\sqrt{3}}\mathrm{I}_i.\mathrm{I}_j + \omega^{ij}_{J_{aniso,0}}(t)\frac{1}{\sqrt{6}}(3I_{iz}I_{jz} - \mathrm{I}_i.\mathrm{I}_j), \tag{13}$$

$$H_D = \sum_{i,j} \omega^{ij}_{D,0}(t)\frac{1}{\sqrt{6}}(3I_{iz}I_{jz} - \mathrm{I}_i.\mathrm{I}_j), \tag{14}$$

$$H_Q = \sum_{i} \omega^{i}_{Q,0}(t)\frac{1}{\sqrt{6}}(3I^2_{iz} - \mathrm{I}^2_i) + \frac{1}{2\omega^{i}_{0}}\left\{\omega^{i}_{Q,-2}(t)\omega^{i}_{Q,2}(t)(2\mathrm{I}^2_i - 2I^2_{iz} - 1)I_{iz}) + \omega^{i}_{Q,-1}(t)\omega^{i}_{Q,1}(t)(4\mathrm{I}^2_i - 8I^2_{iz} - 1)I_{iz}\right\} \tag{15}$$

with i, j representing the concerned spins. ϕ_i is the phase of the RF irradiation (pulse phases), and $\omega^{i}_{RF} = -\gamma_i B^{i}_{RF}$ is the RF nutation frequency. (CS) represents the chemical shift, (J) is the indirect spin–spin coupling, (D) represents the dipole–dipole coupling, and (Q) is the quadrupolar coupling. The symbols γ_i is the gyromagnetic ratio, and J_{iso} and J_{aniso} describe the scalar and anisotropic J coupling, respectively. The aforementioned Hamiltonians are for the Lab frame and can be transformed to the rotor frame R (MAS frame) by the sequence described further. Details of these NMR interactions (eqs. (11–15)) can be found in the literature.[24–26,30,75–77,111] The operator product $\mathrm{I}_i.\mathrm{I}_j$ is truncated to $I_{iz}I_{jz}$ when a coupling occurs between nuclei of different spin species. In eq. (15), the first term represents the first-order quadrupolar coupling, while the second term includes the secular components for the second-order quadrupolar coupling. In the following, we have neglected the second-order term with the secular components. Equation (15) is reduced to

$$H_Q = \sum_{i} \omega^{i}_{Q,0}(t)\frac{1}{\sqrt{6}}(3I^2_{iz} - \mathrm{I}^2_i). \tag{16}$$

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

$$\omega_{\lambda,m'}(t) = \sum_{m=-2}^{2} \omega^{(m)}_{\lambda,m'} e^{im\omega_r t} \tag{17}$$

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

$$\omega^{(m)}_{\lambda,m'} = \omega^{\lambda}_{iso}\delta_{m,0} + \omega^{\lambda}_{aniso}\left\{D^{(2)}_{0,-m}(\Omega^{\lambda}_{PR}) - \frac{\eta^{\lambda}}{\sqrt{6}}\left[D^{(2)}_{-2,-m}(\Omega^{\lambda}_{PR}) + D^{(2)}_{2,-m}(\Omega^{\lambda}_{PR})\right]\right\} d^{(2)}_{-m,m'}(\beta_{RL}) \tag{18}$$

where $\delta_{m,0}$ is the standard Kronecker delta. The constants describing the isotropic (ω^{λ}_{iso}) and the anisotropic (ω^{λ}_{aniso}, η^{λ}) contributions to the Fourier coefficients can be found in the article by Bak *et al.*[76,77] The article also gives a description of the orientation dependence of the anisotropic interactions. The above Hamiltonians are for the magic-angle spinning (MAS) experiment. In the laboratory reference frame, the z-axis is parallel to the static magnetic field. In MAS experiments, the following sequence of transformation is used: $P \rightarrow C \rightarrow R \rightarrow L$. The frames P, R, C, and L represent the principal-axis, the rotor-fixed, the crystal-fixed, and the laboratory-fixed frames, respectively. These frames (P, R, S, and L) are connected by the relation

$$D^{(2)}_{m',m}(\Omega^{\lambda}_{PR}) = \sum_{m"=-2}^{2} D^{(2)}_{m',m''}(\Omega^{\lambda}_{PC}) D^{(2)}_{m'',m}(\Omega_{CR}). \tag{19}$$

The internal Hamiltonians (eqs. (11)–(15)) can also be written in more succinct forms such as those described by Tycko[78] or Schnell and Spiess.[111] For instance, in the form given by Tycko, the Hamiltonian is expressed in terms of $\{\mathrm{Y}_{2m}\}$, which is a basis for an irreducible representation of rotations of the spatial coordinates of the sample, and $\{\mathrm{T}_{2m}\}$, which is a basis for an irreducible representation of rotations of the spin angular momenta. $\{\mathrm{Y}_{2m}\}$ and $\{\mathrm{T}_{2m}\}$ are the second-rank spherical harmonics and the second-rank irreducible tensor operators, respectively. In high field approximation, we

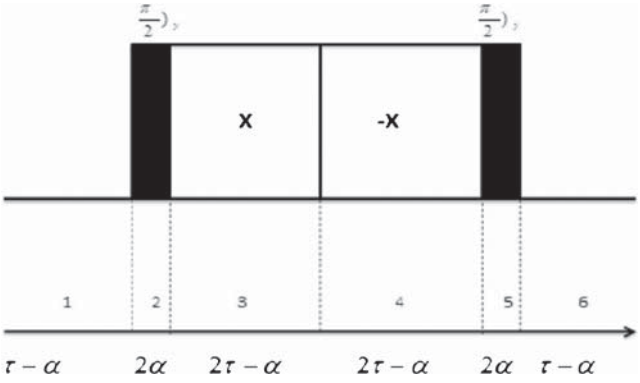


Figure 1. Magic echo sequence for time reversing the evolution of a system of nuclear spins coupled by a dipolar interaction.

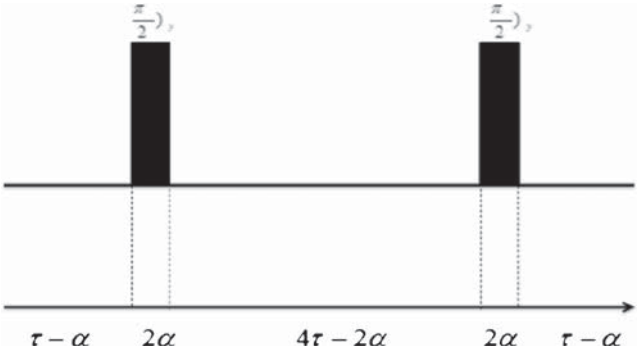


Figure 2. Simple two-pulse quadrupolar echo sequence.

only have the two basis $\{Y_{20}\}$ and $\{T_{20}\}$. For example, the truncated dipole–dipole coupling can be written as

$$H_D = b_{ij}(t)Y_{20}T_{20} \tag{20}$$

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

$$H_Q^{(0)}(t) = \sum_{m=-2}^{2} \left\{ \frac{1}{\sqrt{6}} D_{m0}^{(2)}(\Omega) + \eta \left[D_{m2}^{(2)}(\Omega) + D_{m-2}^{(2)}(\Omega) \right] \right\} D_{0m}^{(2)} \left[\Omega'(t) \right] T_{20}. \tag{21}$$

where η is the asymmetry parameter.

The magic echo sequence (figure 1) is a multiple pulse sequence that has been applied with great success in solid-state NMR. The scheme consists of a period of free evolution of time $\tau - \alpha$, a $\frac{\pi}{2}$ pulse about the y axis, followed by two spin-locking fields of duration $2\tau - \alpha$, and ending with the application of a second $\frac{\pi}{2}$ pulse aboutthe y axis. The cycle is well known in the NMR community to be more efficient than a simple two-pulse quadrupolar echo (solid echo) sequence (figure 2). Specifically, sufficient line-narrowing may be obtained for the magic echo sequence when the free evolution times are made long enough (i.e., about 100 μs). 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 μs). 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.[31,34,99] Figure 3 also represents the magic echo sequence for refocusing the quadrupolar interaction. We presented the results of AHT for various interactions in the solid state when samples are irradiated using the magic echo pulse sequence. The J coupling was neglected and all the durations of the $\frac{\pi}{2}$ pulses were 2α. We consider only the first-order quadrupolar coupling and neglect all the secular components from the second and upper order.

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:[34]

$$\overline{H}_{\Delta\omega}^{0} = \frac{1}{3\tau}\frac{\Delta\omega}{\omega_{RF}} I_y[1 - \cos\omega_{RF}(2\tau - \alpha)] - \frac{1}{3\tau}\frac{\Delta\omega}{\omega_{RF}} I_x[\sin\omega_{RF}(2\tau - \alpha) + \frac{4}{\pi}\omega_{RF}\alpha] \tag{22}$$

$$\overline{H}_{D}^{0} = \omega_D I_z I_z - \omega_D \mathrm{I.I} + \frac{1}{4\tau}\frac{\omega_D}{\omega_{RF}} I_x I_x[2\omega_{RF}(2\tau + \alpha)] + \sin 2\omega_{RF}(2\tau - \alpha)] + \frac{1}{4\tau}\frac{\omega_D}{\omega_{RF}} I_y I_y[2\omega_{RF}(2\tau - \alpha)] - \sin 2\omega_{RF}(2\tau - \alpha)] - \frac{1}{2\tau}\frac{\omega_D}{\omega_{RF}}[I_x I_y + I_y I_x]\sin^2\omega_{RF}(2\tau - \alpha) \tag{23}$$

$$\overline{H}_{\omega_Q}^{0} = \frac{1}{7\tau}\frac{12\alpha\omega_Q}{\pi} I_{x,2} + \frac{4(3\alpha - \tau)\omega_Q}{7\tau} \times \left[I_{x,1}I_{x,1} + I_{y,1}I_{y,1} - 2I_{z,1}I_{z,1} \right] \tag{24}$$

where 2α is the duration of $\pi/2$ pulse width, and ω_D is the dipolar coupling constant. ω_{RF} is the RF field strength, $\Delta\omega$ is the resonance offset, and ω_Q is the quadrupolar coupling constant. The sequence used for the chemical shift and the dipolar interactions consists of a period of free evolution of time $\tau - \alpha$, a $\frac{\pi}{2}$ pulse about the y axis, followed by two spin-locking fields of

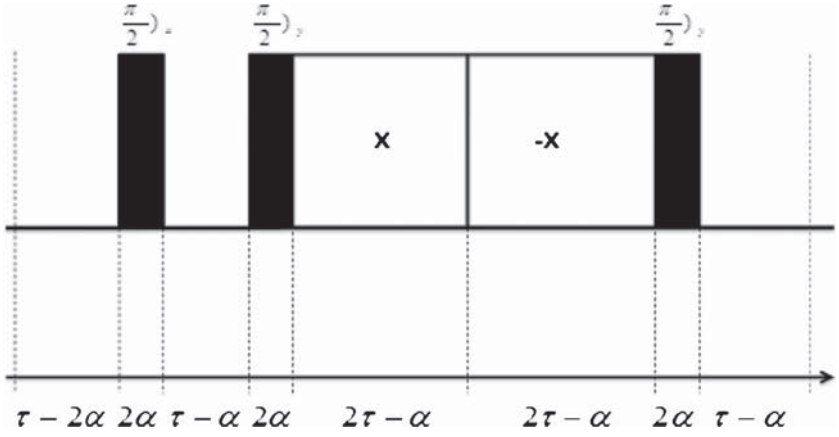


Figure 3. Magic echo sequence for refocusing the quadrupolar interaction.

duration $2\tau - \alpha$, and ending with the application of a second $\frac{\pi}{2}$ pulse about the y axis. The echo occurs at a time $\tau - \alpha$ after the last pulse. For the sequence used in the case of the quadrupolar interaction, a $\frac{\pi}{2}$ pulse about the x axis precedes the magic echo sequence. In the expression of the average Hamiltonian obtained for the quadrupolar interaction, the spin-1 operator formalism developed by Vega and Pines[79] was used. Note that the zero-order term of the average Hamiltonian for the quadrupolar interaction (eq. 21) is obtained when using the magic echo sequence with a $\frac{\pi}{2}$ pulse about the x axis inserted during the first free evolution time as in the figure shown in the previous work by Mananga *et al.*[34]

2.2d *CW decoupling*: We revisit the AHT approach by using the case of heteronuclear decoupling. In the doubly rotating frame of the I and S spins, the truncated dipolar interaction and the RF irradiation with the intensity of ω_1 along the X axis of the I spin for the CW decoupling is given by[84]

$$H = dI_Z S_Z + \omega_1 I_X + \Delta\omega I_Z, \tag{25}$$

where the first term denotes the dipolar interaction, and $\Delta\omega$ represents the off resonance. Following the development of Takegoshi *et al.*[84] the propagator is given by

$$U(t) = e^{-iHt} = e^{(-i\omega_1 I_X t)} T e^{(-i\int_0^t H_0(t_1)dt_1)}, \tag{26}$$

where the relevant Hamiltonianin the toggling frame is given by

$$H_0(t) = A(I_Z \cos\omega_1 t + I_Y \sin\omega_1 t) \tag{27}$$

with

$$A = \Delta\omega + dS_Z. \tag{28}$$

After lengthy calculation, the average Hamiltonian for the first two orders is found to be

$$\overline{H}^{(0)} = 0, \tag{29}$$

$$\overline{H}^{(1)} = \frac{A^2}{2\omega_1} I_X, \tag{30}$$

$$\overline{H}^{(2)} = \frac{A^3}{2\omega_1^2} I_Z. \tag{31}$$

2.2e *Magnus expansion as numerical integrator*: The Magnus expansion can also be used as numerical method for solving eq. (2). One follows a time-stepping advance procedure, from U_0 to obtain the solution $U(t)$. For the sake of simplicity, let us consider a constant time step, $h = \frac{t}{N}$ and $t_j = jh$ with $j = 0, 1, 2..., N$. To obtain u_j, the Magnus expansion is applied in each subinterval $\left[t_{j-1}, t_j\right]$ to the initial condition u_{j-1}. The approximations u_j are computed to the exact values $U(t_j)$. The process involves the following steps:[44,168]

(a) The expansions are truncated according to the order in h to be achieved.
(b) The multivariate integrals in the truncated expansions are replaced by conveniently chosen approximations.
(c) The exponentials of the matrices have to be computed.

Magnus proposed an exponential representation of the solution of eq. (2) in the form

$$U(t) = e^{-i\Omega(t)} U_0, \tag{32}$$

with $\Omega(0) = 0$, where Ω is obtained as an infinite series,

$$\Omega(t) = \sum_{n=1}^{\infty} \Omega_n(t). \tag{33}$$

The average Hamiltonian can be defined by means of an expansion known as Baker–Campbell–Hausdorff expansion or Magnus expansion. In essence, the Magnus expansion yields the solution of the above linear operator equation (eq. (2)) in the exponential form,

where $\Omega(t)$ represents the argument of a unique exponential function obtained as an infinite series.[169] The Ω_1 and Ω_2 obtained from the Magnus expansion or Magnus series suffice to build methods up to order four in h. Blanes and co-workers[44] have shown that the fourth-order Magnus method improves the result achieved by the second order, whereas a higher-order method does not necessarily lead to a better approximation. Next, the averaged matrices procedure is used for different quadrature rules.

$$\begin{aligned} -iH^{(i)}(h) &\equiv \frac{-i}{h^i}\int_{t_n}^{t_n+h}(t-t_{1/2})^i H(t)dt \\ &= -ih\sum_{j=1}^{k} b_j(c_j-\frac{1}{2})^i H_j + O(h^{p+1}), \end{aligned} \tag{34}$$

for $i = 0, 1, ...,$ where $t_{1/2} = t_n + \frac{h}{2}$ and $H_j = H(t_n + c_j h)$. Here, b_j, c_j, $j = 1, ..., k$, are the weights and nodes of a particular quadrature rule of order p, to be chosen by the user.

The first order in the Magnus expansions, $\exp(-iH^{(0)}(h))$, leads to a second-order approximation in the time step h. Using the mid-point rule, we obtain

$$u_{n+1} = \exp(-ihH(t_n + \frac{h}{2}))u_n. \tag{35}$$

Computing $-iH^{(0)}$ and $-iH^{(1)}$ in eq. (34), one can obtain fourth-order methods that provide a good balance between good performance and moderate complexity. A fourth-order Magnus integrator is given by

$$u_{n+1} = \exp(-iH^{(0)} - i[H^{(1)}, H^{(0)}])u_n. \tag{36}$$

Choosing the Gauss-Legendre quadrature rule, we have

$$\begin{cases} H^{(0)} \cong \dfrac{h}{2}(H_1 + H_2) \\ H^{(1)} \cong \dfrac{h\sqrt{3}}{12}(H_2 - H_1) \end{cases}$$

$$\text{where} \begin{cases} H_1 = H\left(t_n + \left(\dfrac{1}{2} - \dfrac{\sqrt{3}}{6}\right)h\right) \\ H_2 = H\left(t_n + \left(\dfrac{1}{2} + \dfrac{\sqrt{3}}{6}\right)h\right) \end{cases} \tag{37}$$

A good perspective of the overall performance of a given numerical integrator is provided by the efficiency diagram.[44,168] This efficiency plot is obtained by carrying out the numerical integrator with different time steps, corresponding to different numbers of evaluations of $H(t)$. For each run, one compares the corresponding approximation with the exact solution, and plots the error as a function of the total number of matrix evaluations. The results are better illustrated in a double logarithmic scale. In that case, the slope of the curves should correspond, in the limit of very small time steps, to (minus) the order of accuracy of the method.

2.3 *Advantages and limitations*

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.[38,39] One has to be able to define a single basic frequency as well as a cycle time of the Hamiltonian. No single cycle time can be defined if the two or more frequencies are incommensurate. For instance, in the MAS experiments, the signal is observed continuously with a time resolution much shorter than the rotor period. Furthermore, because sidebands appear at integer multiples of the basic frequency of Nyquist frequency, they cannot be described in the MAS spectra. They are folded back onto the centre band. A similar effect occurs with radiofrequency irradiation where sidebands are neglected because there are folded back onto the centre band.[26,38,39,105,108–111] Therefore, the method of AHT cannot describe correctly the spectra obtained with MAS. Synchronized experiments and stroboscopic observation after a full cycle time are well described by the technique of AHT.

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 increases. 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 figure 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.

3. Floquet Theory

The FLT introduced to the NMR community in the early 1980s 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 approximavtions.

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, which is of importance in many MAS experimental circumstances to obtain information on anisotropic 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. The author and co-workers of the present study recently have probed 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] 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 artefacts. In the literature, problems with up to four frequencies have been treated, but 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 more frequencies, such as triple-resonance CW radio frequency irradiation under MAS.

3.1 *Useful equations and Propagators*

3.1a *Operator-based Floquet theory*[38,39,94,100,148]: The Floquet operator formalism was introduced for the development of broadband excitation pulses.[148] Operator-based Floquet theory in solid-state NMR gives the following results.

3.1a1 *Single-mode Floquet Hamiltonian*: we assume a periodic time-dependent Hamiltonian that can be expanded in a Fourier series of the form

$$\hat{H}(t) = \sum_{n=-\infty}^{\infty} {}^{(n)}\hat{H} e^{in\omega_m t} \tag{38}$$

where ω_m is the characteristic frequency and the operators ${}^{(n)}\hat{H}$ 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

$$\begin{aligned}\overline{\hat{H}} = {}&{}^{(0)}\hat{H} - \frac{1}{2}\sum_{n\neq 0}\frac{\left[{}^{(-n)}\hat{H}, {}^{(n)}\hat{H}\right]}{n\omega_m} \\ &+ \frac{1}{2}\sum_{n\neq 0}\frac{\left[\left[{}^{(n)}\hat{H}, {}^{(0)}\hat{H}\right], {}^{(-n)}\hat{H}\right]}{(n\omega_m)^2} \\ &+ \frac{1}{3}\sum_{k,n\neq 0}\frac{\left[{}^{(n)}\hat{H}, \left[{}^{(k)}\hat{H}, {}^{(-n-k)}\hat{H}\right]\right]}{kn\omega_m^2} + \ldots\end{aligned} \tag{39}$$

3.1a2 *Bimodal Floquet Hamiltonian*: we assume a periodic time-dependent Hamiltonian that can be expanded in a Fourier series of the form

$$\hat{H}(t) = \sum_{n=-\infty}^{\infty}\sum_{k=-\infty}^{\infty} {}^{(n,k)}H e^{in\omega_r t} e^{ik\omega_m t} \tag{40}$$

where ω_m and ω_r are the characteristic frequencies and the operators ${}^{(n,k)}\hat{H}$ can be viewed as Fourier coefficients of the Hamiltonian with respect to these frequencies. The effective Hamiltonian for a bimodal Floquet Hamiltonian can be obtained to different orders given by

$$\overline{\hat{H}} = \sum_{n_0,k_0} {}^{(n_0,k_0)}\hat{H} - \sum_{n_0,k_0}\frac{1}{2}\sum_{\nu,\kappa}\frac{\left[{}^{(n_0-\nu,k_0-\kappa)}\hat{H}, {}^{(\nu,\kappa)}\hat{H}\right]}{\nu\omega_r + \kappa\omega_m} + \ldots \tag{41}$$

with

$$n_0\omega_r + k_0\omega_m = 0 \tag{42}$$

and

$$\nu\omega_r + \kappa\omega_m \neq 0. \tag{43}$$

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

3.1a3 *Triple-mode Floquet Hamiltonian*: we assume a periodic time-dependent Hamiltonian that can be expanded in a Fourier series of the form

$$\hat{H}(t) = \sum_{n=-\infty}^{\infty}\sum_{k=-\infty}^{\infty}\sum_{l=-\infty}^{\infty} {}^{(n,k,l)}H e^{in\omega_r t} e^{ik\omega_m t} e^{il\omega_p t} \tag{44}$$

where ω_m, ω_r, and ω_p are the characteristic frequencies and the operators ${}^{(n,k,l)}\hat{H}$ 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

$$\overline{\hat{H}} = \sum_{n_0,k_0,l_0} {}^{(n_0,k_0,l_0)}\hat{H} - \sum_{n_0,k_0,l_0}\frac{1}{2}\sum_{\nu,\kappa,\lambda}\frac{\left[{}^{(n_0-\nu,k_0-\kappa,l_0-\lambda)}\hat{H}, {}^{(\nu,\kappa,\lambda)}\hat{H}\right]}{\nu\omega_r + \kappa\omega_m + \lambda\omega_p} + \cdots \tag{45}$$

with

$$n_0\omega_r + k_0\omega_m + l_0\omega_p = 0 \tag{46}$$

and

$$\nu\omega_r + \kappa\omega_m + \lambda\omega_p \neq 0. \tag{47}$$

For triple-mode and higher Floquet problems, resonance conditions involving all frequencies as well as involving only a subset of the frequencies are possible. Such resonance conditions describe problems that are partially resonant and partially non-resonant, depending on the frequencies observed.

3.1b *Matrix-based Floquet theory*: The Floquet Hamiltonian, the density operator, and the detector operator are extensively given in the literature of NMR. Some examples of the matrix-based treatment are given in III.2.3.

3.2 *Applications of Floquet theory*

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 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] described all examples using the Floquet operators introduced by Boender and co-workers.[96] Leskes *et al.*[38] and Scholz *et al.*[39] applied the Floquet theory to investigate numerous cases such as MAS, rotational-resonance recoupling, CW irradiation on a single spin species, DARR and MIRROR recoupling, simultaneous CW irradiation on two different spin species, 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. Let us present here the case of CW decoupling under MAS, the multipole-multimode Floquet theory in NMR, and the Floquet theory of NMR for a single spin.

3.2a *CW decoupling*: We consider again the heteronuclear decoupling in the doubly rotating frame of the I and S spins. The truncated dipolar interaction and the RF irradiation is given by[84]

$$H = dI_Z S_Z + \omega_1 I_X + \Delta\omega I_Z, \tag{48}$$

where ω_1 is the RF irradiation frequency along the X axis of the I spin, $\Delta\omega$ denotes the off resonance, and the first term stands for the dipolar interaction. The propagator is given by

$$U(t) = e^{-iHt} = e^{(-i\omega_1 I_X t)} T e^{\left(-i\int_0^t H_0(t_1)dt_1\right)}, \tag{49}$$

where the relevant Hamiltonian in the toggling frame is given by

$$H_0(t) = A(I_Z\cos\omega_1 t + I_Y \sin\omega_1 t) \tag{50}$$

with

$$A = \Delta\omega + dS_Z. \tag{51}$$

Using eq. (39) of single-mode Floquet Hamiltonian for simplicity reason and after lengthy calculation, the average Floquet Hamiltonian for the first two orders is found to be

$$\overline{H}^{(0)}_{Floquet} = 0, \tag{52}$$

$$\overline{H}^{(1)}_{Floquet} = \frac{A^2}{2\omega_1} I_X, \tag{53}$$

$$\overline{H}^{(2)}_{Floquet} = \frac{A^3}{2\omega_1^2} I_Z. \tag{54}$$

The third-order Floquet expansion is too complicated, and hence it is not calculated.

3.2b *CW decoupling under MAS*: We assume a two-spin system, I-S with rf irradiation on the I spin. The Hamiltonian describing this system, in the rotating frame, is giving by

$$H(t) = \sum_{n=-2}^{2} \omega_S^{(n)} e^{in\omega_r t} S_Z - \sum_{n=-2}^{2} \omega_I^{(n)} e^{in\omega_r t} I_X - \sum_{\substack{n=-2 \\ n\neq 0}}^{2} \omega_{SI}^{(n)} e^{in\omega_r t} 2S_Z I_X + \omega_1 I_{lZ} \tag{55}$$

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

$$\widetilde{H}(t) = e^{(i\omega_1 I_{lZ} t)} H(t) e^{(-i\omega_1 I_{lZ} t)} \tag{56}$$

gives

$$\tilde{H}(t) = \sum_{n=-2}^{2} \omega_S^{(n)} e^{(in\omega_r t)} S_Z - \sum_{n=-2}^{2} \omega_I^{(n)} e^{(in\omega_r t)} \left(\frac{1}{2} I^+ e^{i\omega_1 t} + \frac{1}{2} I^- e^{(-i\omega_1 t)}\right) - \sum_{\substack{n=2 \\ n\neq 0}}^{2} \omega_{SI}^{(n)} e^{(in\omega_r t)} 2S_Z \left(\frac{1}{2} I^+ e^{i\omega_1 t} + \frac{1}{2} I^- e^{(-i\omega_1 t)}\right) \tag{57}$$

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

$${}^{(0,0)}\widetilde{H} = \omega_S^{(0)} S_Z \tag{58}$$

$${}^{(n,0)}\widetilde{H} = \omega_S^{(n)} S_Z \tag{59}$$

$${}^{(0,\pm 1)}\widetilde{H} = -\frac{\omega_I^{(0)}}{2} I^{\pm} - \omega_{SI}^{(0)} S_Z I^{\pm} \tag{60}$$

$${}^{(n,\pm 1)}\widetilde{H} = -\frac{\omega_I^{(n)}}{2} I^{\pm} - \omega_{SI}^{(n)} S_Z I^{\pm} \tag{61}$$

$${}^{(n,\pm 2)}\tilde{H} = 0 \tag{62}$$

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

Decoupling is irradiation outside any resonance condition, i.e., only $n_0 = 0$ and $k_0 = 0$ have to be considered. The effective Hamiltonian is reduced to

$$\begin{aligned}\overline{\hat{H}} &= {}^{(0,0)}\hat{H} - \tfrac{1}{2}\sum_{\nu,\kappa} \frac{\left[{}^{(-\nu,-\kappa)}\hat{H}, {}^{(\nu,\kappa)}\hat{H}\right]}{\nu\omega_r + \kappa\omega_m} + \ldots \\ &= \omega_S^{(0)} S_Z \\ &+ \tfrac{1}{4}\sum_{\nu}\left(\frac{\omega_I^{(\nu)}\omega_I^{(-\nu)} + \omega_{SI}^{(\nu)}\omega_{SI}^{(-\nu)}}{\nu\omega_r + \omega_1} I_Z + \frac{\omega_I^{(\nu)}\omega_{SI}^{(-\nu)} + \omega_{SI}^{(\nu)}\omega_I^{(-\nu)}}{\nu\omega_r + \omega_1} 2S_Z I_Z\right) \\ &- \tfrac{1}{4}\sum_{\nu}\left(\frac{\omega_I^{(\nu)}\omega_I^{(-\nu)} + \omega_{SI}^{(\nu)}\omega_{SI}^{(-\nu)}}{\nu\omega_r - \omega_1} I_Z + \frac{\omega_I^{(\nu)}\omega_{SI}^{(-\nu)} + \omega_{SI}^{(\nu)}\omega_I^{(-\nu)}}{\nu\omega_r - \omega_1} 2S_Z I_Z\right)\end{aligned}$$

Such a result cannot be obtained with average Hamiltonian theory without making assumptions about the ratio of ω_1 and ω_r.

3.2c *Multipole-multimode Floquet theory in NMR*: Nearly three decades ago, Sanctuary proposed the multiple theory approach to describe spin dynamics in NMR.[139–141] The theory treats the spin dynamics in the operator space (Liouville space) with an explicit time-dependent density operator. The Sanctuary approach has been successful in describing the dynamic behaviour and it presents some limitation when dealing with calculations that involve the experimentally detectable magnetization. Furthermore, the approach does not give insights into experiments that involve relaxation such as polarization transfer experiments or multiple-quantum NMR phenomena. Typically, the spin Hamiltonian is described by irreducible tensor operators. However, the spin basis expressed in terms of operators, which are also irreducible under rotations, is still not yet a common practice.[142–144] The multipole formalism exploits this method to the extent of applicability of multiple spins. Sanctuary *et al.*[145] used the following notation for the density operator in the multipole approach:

$$\rho(t) = \frac{1}{\prod_{i=1}^{N}(2I_i+1)} \sum_{k,q,\overline{\alpha}} \Phi_q^{(k)}(\overline{\alpha}, t) T^{(k)q}(\overline{\alpha}), \tag{64}$$

where $\overline{\alpha}$ represents all the quantum numbers described in the operator space.[139] Similarly, the time-independent

Hamiltonian of the system can be expressed on the same basis as that of the density operator:

$$H = \sum_{l,m,\overline{\alpha}} C_{lm(\overline{\alpha})} T^{(l)m}(\overline{\alpha}), \tag{65}$$

where l and m denote the rank and component of the tensor, respectively, with $l \leq 2$ being the standard case in NMR experiments. $C_{lm(\overline{\alpha})}$ are coefficients in the eq. (65) representing the interaction parameters (Zeeman, dipole–dipole, and quadrupolar).

Substituting $\rho(t)$ and H from eqs. (64) and (65) in the following Liouville equation[34–36]

$$i\frac{d\rho(t)}{dt} = [H, \rho(t)], \tag{66}$$

we obtain a set of differential equations,

$$i\frac{d\Phi_q^{(k)}(\overline{\alpha}, t)}{dt} = \sum_{k',q',\overline{\alpha'}} \sum_{l,m,\overline{\alpha_1}} C_{lm}(\overline{\alpha_1}) Tr\left\{T^{(k)-q}(\overline{\alpha}) \times L^{(l)m}(\overline{\alpha_1}) T^{(k')q'}(\overline{\alpha'})\right\} \Phi_{q'}^{(k')}(\overline{\alpha'}, t) \tag{67}$$

where $L^{lm}(\overline{\alpha_1}) = \left[T^{lm}(\overline{\alpha_1})\right]$ represents the Liouville super-operator. Re-writing eq. (67) in the form of a matrix, we have

$$i\frac{d\Phi_q^{(k)}(\overline{\alpha}, t)}{dt} = [A]_{kq,k'q'}\, \Phi_{q'}^{(k')}(\overline{\alpha'}, t). \tag{68}$$

$\Phi_{q'}^{(k')}(\overline{\alpha'}, t)$ are the spin polarizations represented by column vectors. [A] is the tensor representing the super-matrix whose elements can be calculated by using the Wigner–Eckart theorem.[146,147] Details in the evaluation of the super-matrix can be found in the article.[139]

Consider the time-dependent Hamiltonians to solve eq. (68). Floquet theory is appropriated to solve these equations involving the time-dependent coefficients that govern periodic time-dependent phenomena.

However, the application of Floquet theory to multiple spins and quadrupolar systems $\left(I > \frac{1}{2}\right)$ is very often difficult due to the base employed (Fourier transformation). The multipole-multimode Floquet theory (MMFT) offers some possible extensions that yield interesting results in the field of solid-state NMR. The MMFT is useful for providing an intuitive understanding of spin dynamics processes under synchronous and asynchronous time modulations in solid-state NMR experiments. Writing the time-dependent spin Hamiltonian, the density operator, and the Liouville super-operator in Fourier expansions, we have[139]

$$H(t) = \sum_{n_{1\to m}=-\infty}^{\infty} H_{n_{1\to m}} e^{it\omega.n}, \tag{69}$$

$$\rho(t) = \sum_{n_{1\to m}=-\infty}^{\infty} \sum_{k,q,\overline{\alpha}} \Phi_{q,n_{1\to m}}^{(k)}(\overline{\alpha}, t) T^{(k)q}(\overline{\alpha}) e^{it\omega.n} \tag{70}$$

and

$$L(t) = \sum_{n_{1\to m}=-\infty}^{\infty} L(\overline{\alpha_1})_{n_{1\to m}}^{(l)m} e^{it\omega.n} \tag{71}$$

The following notations were used: $n_{1\to m} = n_1, n_2, ..., n_m$, $A_{n_{1\to m}} = A_{n_1,n_2,...,n_m}$, $\omega = \{\omega_1, \omega_2, ..., \omega_m\}$, $n = \{n_1, n_2, ..., n_m\}$, and $\omega.n = \omega_1 n_1 + \omega_2 n_2 + ... + \omega_m n_m$. n_i, and ω_i correspond to the Fourier index and frequency associated with a particular time modulation, respectively. The notation $L(\overline{\alpha_1})_{n_{1\to m}-n'_{1\to m}}^{(l)m}$ includes the interaction coefficients as well as the spin and Fourier operators. The substitution of eqs. (70) and (71) in the Liouville equation produces the following set of coupled differential equations:

$$i\frac{d\Phi(\overline{\alpha}, t)_{q,n_{1\to m}}^{(k)}}{dt} = \sum_{n'_{1\to m}=-\infty}^{\infty} \sum_{k',q',\overline{\alpha'}} \sum_{l,m,\overline{\alpha_1}} \left(Tr\left\{T^{(k)-q}(\overline{\alpha}) \times L(\overline{\alpha_1})_{n_{1\to m}-n'_{1\to m}}^{lm} T^{(k')q'}(\overline{\alpha'})\right\} + (n.\omega)\delta\right) \Phi(\overline{\alpha'}, t)_{q',n'_{1\to m}}^{(k')}. \tag{72}$$

Re-writing the eq. (72) in matrix notation, we have

$$i\frac{d\Phi_{q,n_{1\to m}}^{(k)}(\overline{\alpha}, t)}{dt} = [\,[A]_{kq,k'q'}\,]_{n_{1\to m},n'_{1\to m}} \times \Phi_{q',n'_{1\to m}}^{(k')}(\overline{\alpha'}, t), \tag{73}$$

where $[\,[A]_{kq,k'q'}\,]_{n_{1\to m},n'_{1\to m}}$ represents the super-matrix defined in the infinite dimensional Floquet–Liouville space. The Floquet density operator and the Hamiltonian operator can be written as

$$\rho_F(t) = \sum_{n_{1\to m}=-\infty}^{\infty} \sum_{k,q,\overline{\alpha}} \Phi_{q,n_{1\to m}}^{(k)}(\overline{\alpha}, t) T^{(k)q}(\overline{\alpha}) F_{r_1}^1 F_{r_2}^2 ... F_{r_m}^m, \tag{74}$$

$$H_F = \sum_{r_{1\to m}=-\infty}^{\infty} \sum_{k,q,\overline{\alpha}} T^{(k)q}(\overline{\alpha}) F_{r_1}^1 F_{r_2}^2 ... F_{r_m}^m + \sum_{i=1}^{m} \omega_i N^i. \tag{75}$$

H_F corresponds to the Floquet Hamiltonian. This Floquet Hamiltonian is constructed from the direct product of operators defined by the spin ($T^{(k)q}$) and the Fourier dimensions ($F_{r_m}^m$) corresponding to m^{th} time modulation. The indices q and $r_m$represent the off-diagonality in eqs. (74) and (75). The approach presented here provides a more intuitive and analytical understanding of spin dynamics processes in spite of spanning infinite dimensionality of the problem. An analytical solution given in the form of effective Hamiltonians derived

from contact or van Vleck transformation procedure can substantiate this formalism.[139]

3.2d *Bloch–Siegert shift*: It is valuable to give a simple application of a Floquet Hamiltonian in the calculation of Bloch–Siegert shift in solid-state NMR. We examine a single spin in a strong magnetic field undergoing an RF irradiation. The Hamiltonian in the laboratory frame with an on-resonance RF irradiation is given by

$$H_{Lab}(t) = 2\omega_1 \cos(\omega_{RF} t) I_X + \omega_0 I_Z, \tag{80}$$

where ω_0 is the Larmor frequency of the simple spin, ω_{RF} is the off-resonance value, and ω_1 is the nutation frequency. For a single spin-1/2, the matrix representation by Pauli matrices is written as

$$H_{Lab}(t) = \frac{1}{2}\begin{pmatrix} \omega_0 & 2\omega_1 \cos(\omega_{RF} t) \\ 2\omega_1 \cos(\omega_{RF} t) & -\omega_0 \end{pmatrix}. \tag{81}$$

Using the formula $\cos(\omega_{RF} t) = \frac{e^{(i\omega_{RF} t)} + e^{(-i\omega_{RF} t)}}{2}$, we can write the Fourier expansion of time-dependent Hamiltonian as

$$H_{Lab}(t) = \frac{1}{2}\begin{pmatrix} \omega_0 & 0 \\ 0 & -\omega_0 \end{pmatrix} + \frac{1}{2}\begin{pmatrix} 0 & \omega_1 \\ \omega_1 & 0 \end{pmatrix} e^{(i\omega_{RF} t)} + \frac{1}{2}\begin{pmatrix} 0 & \omega_1 \\ \omega_1 & 0 \end{pmatrix} e^{(-i\omega_{RF} t)} \tag{82}$$

and construct the Floquet Hamiltonian from Fourier coefficients.[83] The approximation by a two-level system equal to

$$H_{Lab}(t) = \frac{1}{2}\begin{pmatrix} \omega_0 - \omega_{RF} + \frac{\omega_1^2}{4\omega_{RF}} & \omega_1 \\ \omega_1 & -(\omega_0 - \omega_{RF} + \frac{\omega_1^2}{4\omega_{RF}}) \end{pmatrix} \tag{83}$$

which gives the following resonance offset and RF irradiation, and the well-documented Bloch–Siegert shift

$$H = (\omega_0 - \omega_{RF}) I_Z + \omega_1 I_X + \omega_R \left(\frac{\omega_1}{2\omega_{RF}}\right)^2 I_Z. \tag{84}$$

Alternatively, Vega's group[38] has recently provided an interesting review of the Floquet theory on the Bloch–Siegert shift. The ω_{RF} frequency was set equal to ω_0 in order to work with a simple form of a Floquet Hamiltonian. For simplicity reasons, the Hamiltonian in the laboratory frame has the form

$$H_{Lab}(t) = -2\omega_1 \cos(\omega_0 t) I_X + \omega_0 I_Z. \tag{85}$$

The Hamiltonian in the toggling frame has a constant part and a time-dependent part expressed as

$$\widetilde{H}(t) = -\omega_1 I_X - \frac{\omega_1}{2} I_- e^{(i2\omega_0 t)} - \frac{\omega_1}{2} I_+ e^{(-i2\omega_0 t)} \tag{86}$$

which can be represented in the Fourier space by

$$\widetilde{H}^F(t) = \sum_{n=0,\pm 2} H_n F_n^Z e^{(in\omega_0 t)}, \tag{87}$$

with

$$H_0 = -\omega_1 I_X, \tag{88}$$

$$H_{\pm 2} = -\frac{\omega_1}{2} I_{\mp} \tag{89}$$

where F_n^Z are the ladder operators in the Zeeman interaction frame. The Floquet representation can be obtained from the above Fourier space.

$$H_F = e^{(-i\omega_0 N^Z t)} \left\{ \tilde{H}^F(t) + \omega_0 N^Z \right\} e^{(i\omega_0 N^Z t)} = \sum_{n=0,\pm 2} H_n F_n^Z + \omega_0 N^Z \tag{90}$$

where N^Z is the number operator in the Zeeman frame. The knowledge of the effective Hamiltonian is important to understand how the pulse sequence work. Using the van Vleck transformation (VVT) to diagonilize the Floquet Hamiltonian,

$$S_F^{(1)} = -i\frac{\omega_1}{2}\left(\frac{I_-}{2\omega_0} F_{2+} - \frac{I_+}{2\omega_0} F_{2-}\right), \tag{91}$$

the effective Hamiltonian to first order can be obtained,[38]

$$H_{eff} \cong H_{eff}^{(0)} + H_{eff}^{(1)} \tag{92}$$

$$H_{eff}^{(0)} = -\omega_1 I_X \tag{93}$$

and

$$H_{eff}^{(1)} = -\frac{\omega_1^2}{4\omega_0} I_Z \tag{94}$$

The first-order correction term is the Bloch–Siegert shift, and is negligible in most of NMR experiments.

3.3 *Advantages and limitations*

Floquet theory delineates the finite-dimensional time-dependent Hilbert (or Liouville) space onto an infinite-dimensional but time-independent Floquet space.[94] Floquet 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 and propagators' subsection (III.1). Operator-based Floquet theory can be easily broadened to multiple incommensurate frequencies with expressions that

are independent to the complete structure of the spin–Hilbert–space Hamiltonian. This operator can be used to study systems with many spins as long as the commutators can be calculated. However, this operator cannot investigate resonance conditions that involve concomitant or synchronous transition in Fourier space and spin space. Matrix-based Floquet description provides a precise description of time-dependent Hamiltonians including the sidebands. The matrix representation and analytical calculations are limited to small spin systems. For multi-mode Floquet calculations, the matrices can become very large, and then require truncation of the Fourier dimensions that introduce artefacts.

4. Fer expansion

The Fer expansion is an alternative to the Magnus expansion and was proposed by Fer more than half a century ago to the study of systems of differential equations.[63,180–185] Because the Fer approach was less known in the scientific community until recently, several information relevant to this expansion have been misleading.[185] For instance, Wilcox in his seminal paper on perturbation theory associated Fer's name with an infinite-product expansion, which is instead a continuous analogue of the Zassenhaus formula.[180] The past two decades and half have witnessed a renewed interest in the Fer expansion, which continues till date.[44,180,183,185] Different directions have been followed. In 2001, Zanna[181] introduced a symmetric version of the Fer expansion by showing that the schemes are time-symmetric for linear problems. While Zanna's general procedure is more complicated than the classical Fer expansion, it prevents numerous advantages such as time-symmetric for linear problems. In 2004, Suying and Zichen presented an algorithm based on Fer's expansion for numerically solving generalized Hamiltonian systems using the Lie transformation technique.[90] Furthermore, these two authors extended their algorithm to any nonlinear dynamic system. Recently, Madhu and Kurur introduced the Fer expansion to the NMR community.[182] For the purpose of illustration, Madhu and co-worker applied the Fer expansion to two simple cases: the Bloch–Siegert shift and the heteronuclear dipolar decoupling.[63] This approach is still in its infancy in the NMR community; therefore, more effort is required to permit the Fer approach to defeat complications including studies that involve non-periodic and non-cyclic cases.[186–188]

As performed for the Magnus expansion, Blanes and co-workers extended the similar analysis to the Fer expansion.[168] These authors attached a matrix factor to the exponential (eq. (3)), and presented the solution in the form

$$U(t) = \exp(-\int_{t_0}^{t} iH(t')dt')M(t, t_0)U_0. \tag{95}$$

The expansion gives an iterative multiplicative prescription to find $M(t, t_0)$.

4.1 *Useful Equations and Propagator*

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

$$U(t) = \prod_{k=1}^{\infty} e^{F_k(t)} = e^{F_1(t)}e^{F_2(t)}.... \tag{96}$$

In the above solution, the argument of the exponential is written as

$$F_1 = -i\int_0^t dt' H(t') \tag{97}$$

and the first-order correction Hamiltonian, which differs from that obtained with Magnus expansion, is given by

$$H_F^1 = e^{-F_1(t)}He^{F_1(t)} - \int_0^1 dx e^{-xF_1(t)}He^{xF_1(t)}. \tag{98}$$

After n iterations, Madhu and co-workers obtained the following results:

$$F_n = -i^n\int_0^t dt' H_F^{(n-1)}(t'), \tag{99}$$

$$H_F^{(0)} = H, \tag{100}$$

$$H_F^{(n)} = -\frac{1}{2}\left[F_n, H_F^{(n-1)}\right] + \frac{1}{3}\left[F_n, \left[F_n, H_F^{(n-1)}\right]\right] + ... \tag{101}$$

where $n = 1, 2, 3, ...$ Eq. (101) shows a series of nested commutators in the expression of $H_F^{(n)}$. The dissimilarity between the Fer expansion and the Magnus expansion stems from the structure of the correction expressions.

The Fer expansion with respect to eqs. (96)–(101) allows the calculation of the results (eqs. (105)–(112)), which involves a series of nested commutators resulting in eq. (106). The results of F_1 obtained for chemical shift, dipolar, and quadrupolar interactions are similar

to the average Hamiltonian, $\overline{H}$, in the sense of the Magnus expansion under the following circumstances:[65]

$$\frac{F_1(\tau_C)}{\tau_C} = \overline{H}, \tag{102}$$

where τ_C is the cyclic time (period of H). The result of eq. (97) and the knowledge of the Hamiltonian $H(t)$ in the Fer approach leads to a straightforward calculation of eq. (101). $H_F^{(1)}$ is the time integral function, which is used in the calculation of F_2. The iteration process can continue easily when the initial values of $F_n(t)$ and $H_F^{(n)}$ are found. One major advantage of the Fer expansion over the AHT (Magnus expansion) is that only an evaluation of nested commutators is required in the calculation of $H_F^{(n)}$ (eq. (101)). The Magnus expansion requires the calculation of nested commutators and their integrals to obtain the correction terms of a Hamiltonian. Blanes *et al.*[44,167,169,172] had proved the convergence of the Fer expansion and showed that the convergence of Fer expansion is much faster than that of Magnus expansion. Blanes and co-workers studied the convergence and error bounds for Fer's expansion.[167] The authors obtained various bounds for Fer ($\xi = 0.8604065$) and Magnus ($\xi = 1.086869$) expansions. These results widen the range $\xi = 0.628$ originally given by Fer,[63] and the range $\xi = 0.693147$ given by Pechukas and Light regarding the Magnus expansion.[189] An upper bound appears already in Fer's original paper. Because for a prescribed precision, more Ω_k's (Magnus argument) are needed than F_k' (Fer argument);[167] hence, in this sense, the Fer expansion converges more rapidly. Furthermore, in the Fer expansion, each argument of the exponentials contains infinity of orders in the expansion parameter, which could greatly favour its convergence rate. Note that Blanes and co-workers used different arguments than those used by Fer,[63] Pechukas and Light.[189] Madhu and Kurur[62] also highlighted the observations such that the calculation of a term like $H_F^{(1)}$ will contain several of the important signatures of the various higher-order terms in Magnus expansion, where all terms need to be calculated independently. In addition, they mentioned that the calculation of the infinite number of commutators in Eq. (101), although appears 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 complementary and provide solutions to the time-dependent Schrodinger equation:

$$\frac{dU}{dt} = -iH(t)U(t). \tag{103}$$

However, the Fer expansion expresses the propagator in the form of an infinite-product of a series of exponentials given by Eq. (96).

4.2 *Applications of Fer expansion*

4.2a *Bloch–Siegert Shift*: In an article by Haeberlen,[31] the untruncated rotating frame Hamiltonian during an on-resonance RF irradiation with $H_{RF} = -2\omega_1 I_X \cos(\omega t + \phi)$ is giving by

$$\begin{aligned} H = H_R^{on}(t) = &-\Delta\omega I_Z - \omega_1 [I_X \cos\phi + I_Y \sin\phi] \\ &-\omega_1 [I_X \cos(2\omega_I t - \phi) + I_Y \sin(2\omega_I t - \phi)] \end{aligned} \tag{104}$$

where ω_I is the Larmor frequency of the I spins.[31,87] $\Delta\omega$ is the off-resonance value, and ω_1 is the RF nutation frequency. The period of $H_R^{on}(t)$ is $\tau_C = \frac{\pi}{\omega_I}$. A direct integration of eq. (97) gives

$$\begin{aligned} F_1 = \int_0^t H dt = &-\Delta\omega I_Z t - \omega_1 t [I_X \cos\phi - I_Y \sin\phi] \\ &-\frac{\omega_1}{2\omega_I} \{I_X [\sin(2\omega_I t - \phi) + \sin\phi] \\ &+I_Y [\cos(2\omega_I t - \phi) - \cos\phi]\}. \end{aligned} \tag{105}$$

Using eq. (101), we can calculate the expression for $H_F^{(1)}$ with the relation $H_F^{(0)} = H$.

$$H_F^{(1)} = \sum_{k=1}^{\infty} \frac{(-1)^k k}{(k+1)!} \left\{F_1^k(t), H\right\}. \tag{106}$$

In eq. (106), the repeated commutator bracket $\left\{F_1^k(t), H\right\}$ is defined by[88]

$$\left\{F_1^0(t), H\right\} = H \tag{107}$$

and

$$\left\{F_1^{n+1}(t), H\right\} = \left[F_1(t)\ , \left\{F_1^n(t), H\right\}\right] \tag{108}$$

The first commutator of eq. (106) is $-\frac{1}{2}[F_1(\tau_C), H]$. The computed coefficient term of $(-I_Z)$ is the well-documented Bloch–Siegert shift given by $\omega_I(\frac{\omega_1}{2\omega_I})^2$.

4.2b *Heteronuclear dipolar decoupling*: Haeberlen[31] and Ernst[87] presented the Hamiltonian in the doubly rotating frame of the I spin by

$$\begin{aligned} H(t) = &d_{IS} S_Z (I_Z \cos\omega_{1I} t - I_Y \sin\omega_{1I} t) \\ &-\Delta\omega (I_Z \sin\omega_{1I} t - I_Y \cos\omega_{1I} t) \end{aligned} \tag{109}$$

where d_{IS} is the dipolar coupling constant. $\Delta\omega$ is the off-resonance value, and ω_{1I} is the nutation frequency of the RF irradiation on the I spins. $H(t)$ is the periodic

Hamiltonian with period $\tau_C = \frac{2\pi}{\omega_{1I}}$. A direct integration of eq. (97) results in

$$F_1(t) = \int_0^t H dt = \tfrac{1}{\omega_{1I}} d_{IS} S_Z (I_Z \sin\omega_{1I} t + I_Y \cos\omega_{1I} t) - \tfrac{\Delta\omega}{\omega_{1I}} (I_Z \cos\omega_{1I} t + I_Y \sin\omega_{1I} t) + \tfrac{1}{\omega_{1I}} d_{IS} S_Z I_Y - \tfrac{\Delta\omega}{\omega_{1I}} I_Y \quad (110)$$

From eq. (110) and from the evaluation of the first commutator given by $-\frac{1}{2}[H, F_1(\tau_C)]$, both Madhu et al.[62] and Haeberlen[31] obtained the result

$$H_F^{(1)} \cong -\frac{1}{2\omega_{1I}} d_{IS}^2 S_Z^2 I_X + \frac{\Delta\omega}{\omega_{1I}} d_{IS} S_Z I_X - \frac{\Delta\omega^2}{2\omega_{1I}} I_X \quad (111)$$

Madhu *et al.*[62] obtained the expression of $H_F^{(1)}$ for the second commutator in eq. (101) when dealing with on-resonance conditions

$$H_F^{(1)} \cong -\frac{1}{2\omega_{1I}} d_{IS}^2 S_Z^2 I_X + \frac{1}{6} \frac{d_{IS}^3 S_Z^3}{\omega_{1I}^2} I_Z. \quad (112)$$

In eq. (112), the second term on the right-hand side is derived 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.

4.2c *Interactions in solid-state NMR when irradiated with magic echo pulse sequence*: Using the Fer expansion, one can easily calculate the integrations of the toggling frames of the various Hamiltonians described above to obtain the function $F_1(t)$. The following results are obtained for the chemical shift, dipolar and quadrupolar interactions.[64]

$$F_{1(CS)}(t) = \frac{2\Delta\omega}{\omega_{RF}} I_x(\cos\omega_{RF} t - 1) + \frac{\Delta\omega}{\omega_{RF}} [-I_x(\sin\omega_{RF} t + \sin\omega_{RF}(t-\xi) + \sin\omega_{RF}\xi) + I_y(-\cos\omega_{RF} t + 1 - \cos\omega_{RF}(t-\xi) + \cos\omega_{RF}\xi)] \quad (112)$$

$$\begin{aligned} F_{1(D)} = {} & 2\omega_D(3I_zI_z - \mathrm{I.I})t \\ & + \frac{\omega_D}{\omega_{RF}}\{3I_zI_z\left(\frac{1}{2}\sin 2\omega_{RF}t + \omega_{RF}t\right) \\ & + I_xI_x\left(-\frac{1}{2}\sin 2\omega_{RF}t + \omega_{RF}t\right) - 4\omega_{RF}\mathrm{I.I}t \\ & + \frac{3}{2}I_xI_x\left(\frac{1}{2}\sin 2\omega_{RF}t + \omega_{RF}t\right. \\ & \left. + \frac{1}{2}\sin 2\omega_{RF}(t-\xi) + \omega_{RF}(t-\xi)\right) + \\ & + \frac{3}{2}I_yI_y\left(-\frac{1}{2}\sin 2\omega_{RF}t + \omega_{RF}t\right. \\ & \left. - \frac{1}{2}\sin 2\omega_{RF}(t-\xi) + \omega_{RF}(t-\xi)\right) \\ & - \frac{3}{4}(I_xI_y + I_yI_x)(\cos 2\omega_{RF}t + \cos 2\omega_{RF}(t-\xi))\} \end{aligned} \quad (113)$$

$$\begin{aligned} F_{1(Q)} = {} & \omega_Q(12I_{z,1}I_{z,1} + 24I_{y,1}I_{y,1} - 9\mathrm{I.I})t \\ & + \frac{\omega_Q}{2\omega_{RF}}\{(12I_{z,1}I_{z,1} + 12I_{y,1}I_{y,1} + 24I_{x,1}I_{x,1}) \\ & \left(\frac{1}{2}\sin 2\omega_{RF}t + \omega_{RF}t\right) + (12I_{z,1}I_{z,1} + 24I_{y,1}I_{y,1} \\ & + 12I_{x,1}I_{x,1})\left(-\frac{1}{2}\sin 2\omega_{RF}t + \omega_{RF}t\right) \\ & 12I_{x,1}I_{x,1}\left(\frac{1}{2}\sin 2\omega_{RF}(t-\xi) + \omega_{RF}(t-\xi)\right) \\ & + 12I_{z,1}I_{z,1}\left(-\frac{1}{2}\sin 2\omega_{RF}(t-\xi) + \omega_{RF}(t-\xi)\right) \\ & - 6(I_{y,2} + I_{z,2})\cos 2\omega_{RF}t + 6I_{y,2}\cos 2\omega_{RF}(t-\xi)\} \end{aligned} \quad (114)$$

where

$$\xi = 2\tau - \alpha. \quad (115)$$

To proceed further, $H_F^{(1)}$ can be computed using the value of $F_1(t)$. The iteration process can continue easily when the initial values of $F_n(t)$ and $H_F^{(n)}$ are calculated.[64]

While the Magnus expansion is now well developed and has been successfully applied to NMR, the Fer expansion instead has had an odd history. Unlike the Magnus expansion, which has had a persistent impact in the scientific literature since the 1954 seminal paper by Magnus, much less attention has been paid to the Fer expansion. From the 1958 seminal paper of Fer,[63] the work by Klarsfeld and Oteo in 1989[185] seems to be the first application of the Fer expansion to any physical problem. The authors applied the FE to two simple problems of physical interest: the time-dependent forced harmonic oscillator and a particle of spin-1/2 in a constant magnetic field.[185] Some authors misquoted the seminal Fer paper (1958) as a reference for the Magnus expansion.[190] Other authors associated Fer's name with an alternative approach.[88] In NMR for instance, it is only recently (2006) that a tentative of introduction of the FE to the NMR community was done by Madhu and Kurur.[62] Unlike the FE, instead the Magnus expansion was introduced to NMR nearly half a century ago. Eqs. (112)–(115) are the results from a limited endeavour to present the Fer expansion for the computation of effective Hamiltonians.[62]

4.2d *Fer Expansion as Numerical Integrator*: The Fer expansion can also be applied as a numerical method to solve eq. (2). Imitating the same three-steps methodology as previously done for the case of Magnus expansion, the Fer expansion inspection comes to

$$F_k(h) = O(h^{2^k - 1}) \quad (116)$$

where

$$k = 1, 2, ... \tag{117}$$

The functions F_1, F_2 serve to construct methods up to order six in h[44]. The methodology of the Fer expansion as numerical integrator is similar to the Magnus expansion with the difference that a fourth-order Fer integrator yields

$$u_{n+1} = \exp(-iH^{(0)})\exp(-i\left[H^{(1)}, H^{(0)}\right] - \frac{i}{2}\left[H^{(0)}, \left[H^{(0)}, H^{(1)}\right]\right])u_n. \tag{118}$$

4.3 *Advantages and Limitations*

The Fer expansion[180–185] is a sophisticated approach that involves the product of exponentials for the computation of effective propagators and effective Hamiltonians in time-dependent problems, which are of a regular phenomenon in solid-state NMR. In the Magnus expansion, the evaluation of nested commutators and their integrals is required to compute the correction terms of a Hamiltonian. However, the Fer expansion needs only the evaluation of nested commutators. The computation of the infinite number of commutators, although appearing impressive, may turn out to be straightforward to manipulate in most experimentally fascinating cases due to the rapid convergence and the minor value of many of the commutators. The rapid convergence of the Fer expansion can be explained by its lower bounds compared to the Magnus expansion.[73] This has been highlighted previously (section IV.1.). Furthermore, the Fer expansion can also be used as a numerical method for solving the time-dependent Schrodinger equation.

5. Floquet–Magnus expansion

Recently, Mananga and Charpentier introduced the Floquet–Magnus expansion approach to nuclear magnetic resonance.[18,82] The approach was developed by Casas and co-workers[166] as a Magnus expansion well suited for the Floquet theory of linear ordinary differential equations with periodic coefficients. This method is unique in spin physics and useful to shed new light on AHT and FLT.[18–28,44,166–185] The FME scheme is a new theoretical tool that explains spin dynamics in solid-state NMR. Furthermore, the FME is an extension of the popular Magnus expansion and average Hamiltonian theory and calculations could be developed in a finite-dimensional Hilbert space instead of an infinite-dimensional space within the Floquet theory. This approach governs the spin dynamic systems 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.

$$H^{(0)}_{AHT} = H^{1}_{eff(FT)} = H_{1(FME)} = H_0. \tag{119}$$

The FME approach can be considered an improved AHT or a new version of FLT, which could be very useful in simplifying calculations and providing a more intuitive understanding of spin dynamics processes. The FME is essentially distinguished from other theories with its famous function $\Lambda_n(t)$ $(n = 1, 2, 3, ..)$, which facilitates the evaluation of the spin behaviour in between the stroboscopic observation points. The $\Lambda_n(t)$ functions 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. Therefore, the function $\Lambda_n(t)$ can be viewed as the argument of the operator that introduces the frame that varies under the time-independent Hamiltonian F. The relationship with the regular Magnus expansion can be obtained from[18]

$$\frac{\Omega(T)}{T} = e^{-i\Lambda(0)} F e^{i\Lambda(0)}. \tag{120}$$

Eq. (120) points out that it is only in the case

$$\Lambda(0) = 0, \tag{121}$$

that the FME gives the AHT as provided by the ME. Eq. (120) is the general approach of the AHT called FME, which gives also the option of

$$\Lambda(0) \neq 0. \tag{122}$$

The function $\Lambda_n(t)$ is connected to the appearance of features such as spinning sidebands in MAS. The FME general formulas are given in the next section.[18] The evaluation of $\Lambda_n(t)$ is useful in many different ways such as in rotating experiment of NMR. The $\Lambda_n(t)$ function can be used to quantify the level of productivity of double quantum terms.[84,85] The Floquet–Magnus expansion is more appropriate for sample-spinning experiments. The technique of AHT was found to be less descriptive for rotating systems that were more conveniently described using Floquet theory.[45] Like the FLT, the FME describes the time evolution of the spin system at all times. In the article by Mananga and Charpentier,[18] we showed that the lowest-order term F_1 as provided by AHT, FLT, and FME is identical. Next, using the FME, we computed for each interaction the first-order function $(\Lambda_1(t))$ that provides an easy way for evaluating the spin system evolution. This function $\Lambda_1(t)$ is connected to the appearance of features like spinning sidebands in MAS. The evaluation of $\Lambda_1(t)$ is

important 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 $\Lambda_1(t)$ is available only in the FME approach. It could be used to explain the spin dynamics in solid-state NMR.

5.1 *Useful Equations and Propagators*

Considering the initial conditions to be $\Lambda(0) = 0$ (i.e., $P(0) = I$), Blanes and co-workers derived explicitly the first set of Floquet–Magnus expansion equations.[44,66,166] These 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 by[18]

$$\Lambda_n(t) = \Lambda_n(0) + \int_0^t G_n(x)dx - tF_n, \tag{123}$$

with

$$F_n = \frac{1}{T}\int_0^T G_n(x)dx. \tag{124}$$

The first-order contributions to the FME give explicitly

$$G_1(x) = H(x), \tag{125}$$

$$G_2(x) = -\frac{i}{2}\left[H(x) + F_1, \Lambda_1(x)\right], \tag{126}$$

$$\begin{aligned} G_3(x) \;=\; & -\frac{i}{2}\left[H(x) + F_1, \Lambda_2(x)\right] - \frac{i}{2}\left[F_2, \Lambda_1(x)\right] \\ & - \frac{1}{12}\left[\Lambda_1(x), \left[\Lambda_1(x), H(x) - F_1\right]\right] \end{aligned} \tag{127}$$

Symbolic calculation software can enable formal derivation of higher-order terms. In the above equations (eqs. (123–127)), the $\Lambda_n(t)$ functions with $n = 1, 2, 3, \ldots$, represent the nth-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] The FME propagator is given by

$$U(t) = P(t)\exp\{-itH_F\}\,P^{+}(0). \tag{128}$$

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

$$P(t) = \exp\{-i\Lambda(t)\}. \tag{129}$$

5.2 *Applications of the Floquet–Magnus expansion*

5.2a *Simple cases*:

5.2a1 *Common form of a Hamiltonian in solid-state NMR*: Here, we revisited the static perturbation theory,[18,68,81] 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, let us consider the Hamiltonian

$$H = \omega_0 I_Z + \lambda\sum_m (-1)^m R_{2,-m}T_{2,+m} \tag{130}$$

where $\omega_0 I_Z$ 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 $\left[I_Z, T_{2,m}\right] = mT_{2,m}$. The static perturbation theory (SPT) in terms of the irreducible tensor operators gives the diagonal Hamiltonian (with respect to $\omega_0 I_Z$)

$$\begin{aligned} H_{SPT} = \; & \omega_0 I_Z + \lambda R_{2,0}T_{2,0} \\ & + \frac{\lambda^2}{2\omega_0}\sum_{m\neq 0}\frac{R_{2,m}R_{2,-m}}{m}\left[T_{2,m}, T_{2,-m}\right]. \end{aligned} \tag{131}$$

Goldman [68] discussed the discrepancies between AHT and FT in the rotating frame representation where the Hamiltonian becomes time-dependent such as

$$\widetilde{H}(t) = e^{+i\omega_0 I_Z t}He^{-i\omega_0 I_Z t} = \lambda\sum_m (-1)^m R_{2,-m}T_{2,m}e^{im\omega_0 t}. \tag{132}$$

The above FME eqs. (123) and (124) produce the first-order terms

$$F_1 = \lambda R_{2,0}T_{2,0} \tag{133}$$

$$\Lambda_1(t) = \lambda\sum_{m\neq 0}(-1)^m\frac{R_{2,-m}T_{2,+m}}{im\omega_0}e^{im\omega_0 t} \tag{134}$$

whereas the AHT (stroboscopic detection) produces[18]

$$\Lambda_1(t) = \lambda\sum_{m\neq 0}(-1)^m\frac{R_{2,-m}T_{2,+m}}{im\omega_0}(e^{im\omega_0 t} - 1) \tag{135}$$

Also, the FME scheme[18] gives identical results for the second-order term as the SPT theory

$$F_2 = \frac{\lambda^2}{2\omega_0}\sum_{m\neq 0}\frac{R_{2,m}R_{2,-m}}{m}\left[T_{2,m}, T_{2,-m}\right]. \quad (136)$$

This is proof that FME provides an expansion in the rotating frame, which is in agreement with the static perturbation theory and Van Vleck transformations. However, this is different for the Magnus expansion. The agreement can be viewed as the connection between the FME and SPT propagators as explained in the original article.[18]

5.2a2 *Extension to multimode Hamiltonian*: The application of FME to multimode Hamiltonian with frequencies $\vec{\omega} = (\omega_1, ..., \omega_N)$ is straightforward. Considering the generalized Fourier expansion of the Hamiltonian ($\vec{\omega} = (\omega_1, ..., \omega_N)$ represented by the frequency indices)

$$H(t) = \sum_{\vec{m}} H_{\vec{m}} \exp(-i\vec{m}.\vec{\omega}t) \quad (137)$$

we obtain

$$\Lambda_1(t) = \sum_{\vec{m}.\vec{\omega}\neq 0}\frac{H_{\vec{m}}}{i\vec{m}.\vec{\omega}}e^{-i\vec{m}.\vec{\omega}t} \quad (138)$$

and

$$F_1 = \sum_{\vec{m}.\vec{\omega}=0} H_{\vec{m}}. \quad (139)$$

Similarly, the computation of the 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.

5.2b *Investigation of the Effect of Finite Pulse Errors on BABA Pulse Sequence*: The basic BABA pulse sequence shown in figure 4 is built as

$$\left[\left(90^0_X - \frac{\tau_R}{2} - 90^0_{\bar{X}}\right)\left(90^0_X - \frac{\tau_R}{2} - 90^0_{\bar{Y}}\right)\right],$$

where the 90° pulses in the middle of the pulse sequence and between different cycles are placed Back-to-Back (BABA). As shown below, the timing of the BABA sequence is important for full synchronization of the sample rotation that can generate a pure DQ Hamiltonian. Using the FME, we calculated the degree to which the dipolar Hamiltonian leads to the maximum strength of the DQ Hamiltonian as a result of irradiating an ensemble of dipolar-coupled spin-pairs with the basic and the broadband BABA pulse sequence acting on τ_R. The BABA pulse sequence acting on one rotor period τ_R is constructed from four rf pulses, with flip angles $\left\{\frac{\pi}{2}, \frac{\pi}{2}, \frac{\pi}{2}, \frac{\pi}{2}\right\}$ and rf phases $\{X, -X, Y, -Y\}$.

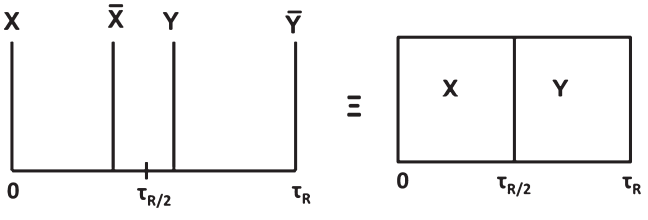


Figure 4. BABA pulse sequence with $\delta - pulse$ width.

In figure 5, the relation $\theta_X(t) = 1 - \theta_Y(t)$ is valid only during the interval where $\theta(t)$ acted. We investigated the finite-pulse-widths effects for the BABA pulse sequence using the Floquet–Magnus expansion approach.[67,102] We studied the case $m = 1$and considered a system of two spins. Only DQ terms are considered for the function $\Lambda_1(t)$. We considered the simple case where the rotations are:

$$\alpha^{ij} = \beta^{ij} = \gamma^{ij} = 0.$$

The coefficient C_n^{ij} are $C_1 = \frac{-1}{\sqrt{3}}\sin(\theta)\cos(\theta)e^{-i\phi}$, $C_{-1} = 0$, $C_2 = \frac{1}{(2\sqrt{6})(\sin^2(\theta)e^{-2i\phi})}$, $C_{-2} = 0$. 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

$$\Lambda_1(t) = \frac{3}{2\sqrt{6}}b_{ij}\left[a_{-1}C_1(\frac{\tau+4\tau_p}{2})\psi + a_{-2}C_2(\frac{\tau_R+4\tau_p}{2})\psi\right](I_{YY}-I_{XX}) \quad (140)$$

where

$$\psi = \frac{t}{\tau_R}, \quad (141)$$

$$\phi = \frac{2\tau_p}{\tau_R} \quad (142)$$

$$a_{-1} = \frac{-1}{2\pi i}e^{-i\pi(1+\phi)}\left[e^{-i\pi(1-2\phi)} - 1\right]. \quad (143)$$

and

$$a_{-2} = \frac{-1}{4\pi i}e^{-i2\pi(1+\phi)}\left[e^{-i2\pi(1-2\phi)} - 1\right] \quad (144)$$

which lead to

$$\frac{\Lambda_1(\psi,\phi)}{b_{ij}\tau_R} = \frac{3}{2\sqrt{6}}(-a_{-1} + \frac{1}{2\sqrt{2}}a_{-2})(\frac{1}{2}+\phi)\psi(I_{YY}-I_{XX}) \quad (145)$$

As reported by Mananga and Reid,[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 eq. (145). First, the plot of the function $\frac{\Lambda_1(t)}{b_{ij}\tau_R}$

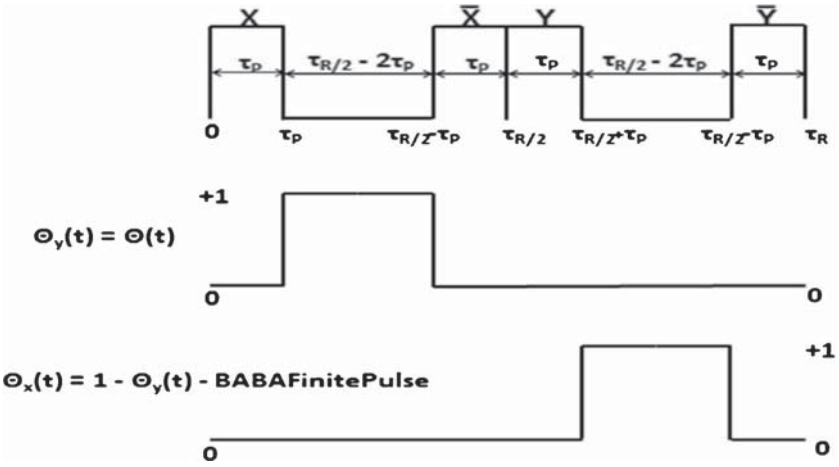
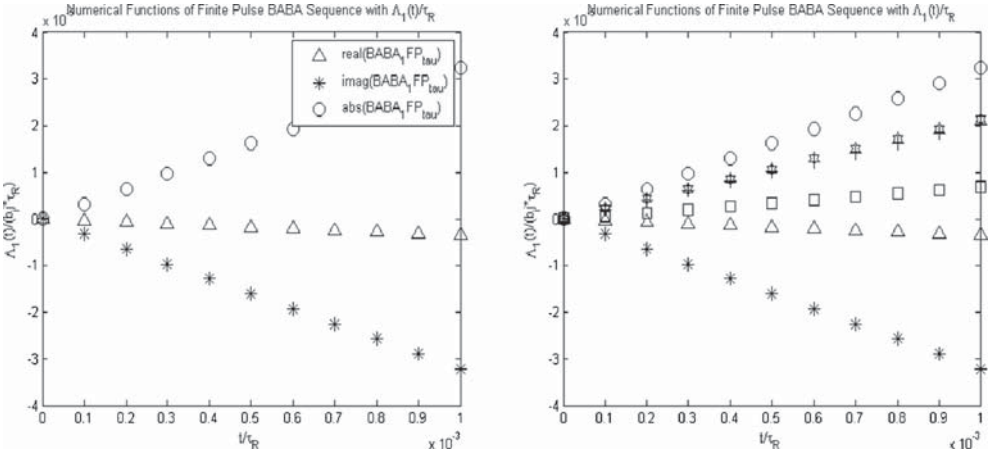


Figure 5. BABA pulse sequence with finite pulse width.



a) For $\phi = 0.1$ b) For $\phi = 0.1$ and $\phi = 0.606$

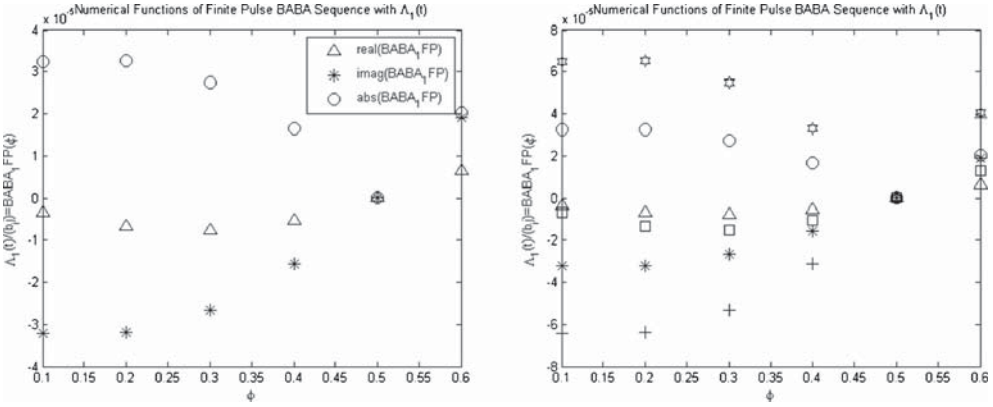
Figure 6. Numerical Functions of Finite Pulse BABA Sequence with $\frac{\Lambda_1(t)}{b_{ij}\tau_R}$ versus $\psi = \frac{t}{\tau_R}$.

versus $\psi = \frac{t}{\tau_R}$, with $\phi = \frac{2\tau_p}{\tau_R}$ kept constant, corresponds to figure 6. The plot of $\frac{\Lambda_1(t)}{b_{ij}\tau_R}$ versus $\phi = \frac{2\tau_p}{\tau_R}$, while keeping the time t constant, corresponds to figure 7.

5.2b1 *Analysis of Figures*: Figure 6 (a) is a plot of the dimensionless function $\frac{\Lambda_1(t)}{b_{ij}\tau_R}$ for BABA pulse sequence with finite pulse widths versus the dimensionless number $\psi = \frac{t}{\tau_R}$, for $\phi = 0.1$. Figure 6 (b) is the plot of the same function $\frac{\Lambda_1(t)}{b_{ij}\tau_R}$ versus $\psi = \frac{t}{\tau_R}$, for the two cases: $\phi = 0.1$ and $\phi = 0.606$. Due to the complexity of the function $\frac{\Lambda_1(t)}{b_{ij}\tau_R}$, we plotted the real, imaginary, and absolute parts separately as a function of ψ. In figure 6 (b), the symbols 'square', 'plus', and 'hexagram' represent the real, imaginary, and absolute parts, respectively, of the function $\frac{\Lambda_1(t)}{b_{ij}\tau_R}$ for $\phi = 0.606$. These functions depend on the DQ terms. Therefore, the investigation 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 represents a quantitative aspect of the amplitude of the DQ coherence as a function of ψ. The size of the function $\frac{\Lambda_1(t)}{b_{ij}\tau_R}$ determines the amplitude of the DQ coherence, which indicates the degree of efficiency of the scheme. A closer look at figures 6 and 7 (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 $\delta - pulse\ sequences$,

$$\left|\frac{\Lambda_1(t)}{b_{ij}\tau_R}\right|_{finite-pulse} < \left|\frac{\Lambda_1(t)}{b_{ij}\tau_R}\right|_{\delta-pulse} \tag{146}$$

as expected. Figure 7 (a) shows the plot of the function $\frac{\Lambda_1(t)}{b_{ij}\tau_R}$ for BABA pulse sequence with finite pulse



a) For t = 1 ms b) For t = 1 ms and t = 2 ms

Figure 7. Numerical Functions of Finite Pulse BABA Sequence with $\frac{\Lambda_1(t)}{b_{ij}}$ versus $\phi = \frac{2\tau_p}{\tau_R}$.

widths versus the dimensionless number $\phi = \frac{2\tau_p}{\tau_R}$, for $t = 1$ ms. Figure 7 (b) shows the plot of the same function $\frac{\Lambda_1(t)}{b_{ij}}$ versus $\phi = \frac{2\tau_p}{\tau_R}$ for the two cases: $t = 1$ ms and $t = 2$ ms. As with figure 6, due to the complexity of the function $\frac{\Lambda_1(t)}{b_{ij}}$, real, imaginary, and absolute parts are plotted separately as functions of ϕ. In figure 7 (b), the symbols 'square', 'plus', and 'hexagram' represent, respectively, the real, imaginary, and absolute parts of the function $\frac{\Lambda_1(t)}{b_{ij}}$ for $t = 2$ ms. These functions depend on the DQ terms. We remark 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, which corresponds to the delta-pulse sequence. However, when $\phi = 0.5$ corresponding to $\tau_p = \frac{\tau_R}{4}$, we have $\frac{\Lambda_1(t)}{b_{ij}} = 0$. The strength of the DQ terms decreases, cancels and builds 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 $\Lambda_1(t)$ 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 much appropriated to forecast the cases of decoupling.

5.2b2 *Numerical Analysis of BABA*: Let us consider a system of two spins, for $m = 1$. We only examine the DQ terms for the functions $\Lambda_1(t)$ and $\Lambda_2(t)$. We assumed the simple case where the rotations are: $\alpha^{ij} = \beta^{ij} = \gamma^{ij} = 0$.

The coefficients C_n^{ij} are $C_1 = \frac{-1}{\sqrt{3}}\sin\theta\cos\theta e^{-i\Phi}$, $C_{-1} = 0$, $C_2 = \frac{1}{2\sqrt{6}}\sin^2\theta e^{-2i\Phi}$ and $C_{-2} = 0$. For example, with $\theta = \frac{\pi}{4}$ and $\Phi = 0$, the coefficients are $C_1 = \frac{-1}{2\sqrt{3}}$ and $C_2 = \frac{1}{4\sqrt{6}}$. The functions $\Lambda_1(t)$ and $\Lambda_2(t)$ in terms of the rotor period are given by

$$\frac{\Lambda_1(t)}{b_{ij}\tau_R} = BABA_1(\varphi) = \frac{1}{\left(16\sqrt{2}\pi\right)\left(i - \frac{1}{\pi\sqrt{2}}\right)(e^{-12\pi\varphi} - 1)\left(I_{YY}^{ij} - I_{XX}^{ij}\right)} \quad (147)$$

$$\frac{\Lambda_2(t)}{b_{ij}^2\tau_R^2} = BABA_2(\varphi) = \{\frac{1}{768}[\frac{-1}{2}(e^{-4\pi i\varphi} - 1) + (e^{-i2\pi\varphi} - 1)] + \frac{i}{768\pi^3}[\frac{1}{8\sqrt{2}}(e^{-i4\pi\varphi} - 1) - (e^{-i2\pi\varphi} - 1)]\}(I_{YY}^{ij} - I_{XX}^{ij}) - \{\frac{1}{6144\pi^2}(1 - \frac{1}{2\sqrt{2}})(e^{i2\pi\varphi} + e^{-i2\pi\varphi} - 2)\}(I_{YY}^{ij} - I_{XX}^{ij}) \quad (148)$$

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

5.2b3 *Analysis of Figures*: Figure 8 shows the plot of both functions $\Lambda_1(t)$ and $\Lambda_2(t)$ versus φ. Due to the complexity of these functions ($\Lambda_1(t)$ and $\Lambda_2(t)$), real, imaginary, and absolute parts are plotted separately as functions of φ. These functions depend on the DQ terms. Therefore, the study of the amplitude of DQ terms can be considered as a viable approach for controlling the complex spin dynamics of a spin system evolving under the dipolar interaction of BABA pulse sequence. The plot can be considered as a quantitative representation of the amplitude of the DQ coherence as a function of φ. The size of $BABA_1(\varphi) = \frac{\Lambda_1(t)}{b_{ij}\tau_R}$ determines the amplitude of the DQ coherence, which indicates the degree of efficiency of the scheme. Figure 8 shows the graphs of the functions $\frac{\Lambda_1(t)}{b_{ij}\tau_R} = BABA_1(\varphi)$, $\frac{\Lambda_2(t)}{b_{ij}^2\tau_{ij}^2} = BABA_2(\varphi)$ and $(BABA_1(\varphi),\ BABA_2(\varphi))$ as a function of $\varphi = \frac{t}{\tau_R}$. A closer look at figure 8 shows that the magnitude of $BABA_2(\varphi)$ is smaller than the

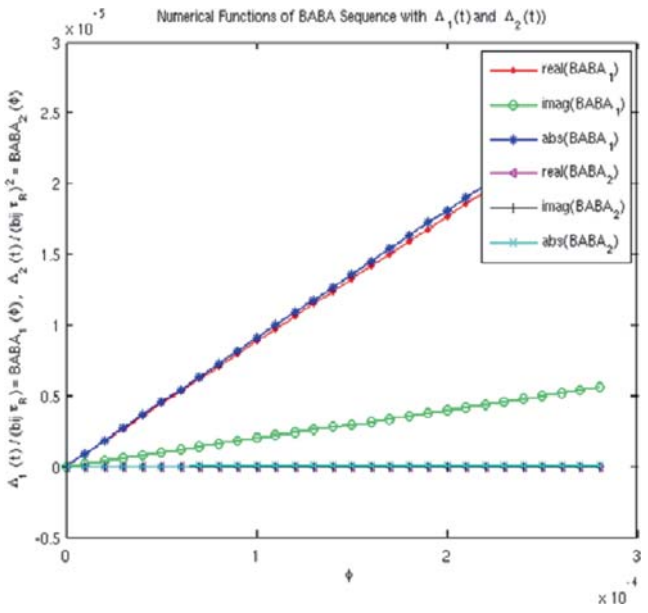


Figure 8. Numerical functions of BABA sequence with $\Lambda_1(t)$ and $\Lambda_2(t)$ versus $\phi = \frac{2\tau_p}{\tau_R}$.

magnitude of $BABA_1(\varphi)$, that is, $|\frac{\Lambda_2(t)}{b_{ij}^2\tau_R^2}| < |\frac{\Lambda_1(t)}{b_{ij}\tau_R}|$ as expected. As a result, $\Lambda_2(t)$ will be less useful in many cases. We can also observe that all curves are strictly monotonous. Therefore, the strength of the DQ terms increases continuously with time and no decoupling conditions occur in the BABA pulse sequence.

5.2c *Criteria to average out chemical shift anisotropy for BABA*: In a recent work[64,65] we showed that the condition for the CSA to be averaged out in each rotor period τ_R can be obtained by applying the first contribution terms of the Floquet–Magnus expansion to the chemical shift anisotropy when irradiated with the BABA pulse sequence. 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 form:

$$H_{CSA}(t) = \sum_i \delta^i_{CSA}(t) I^i_Z \tag{149}$$

where

$$\delta^i_{CSA}(t) = \sum_{n=-2}^{+2} f^i_n(\alpha, \beta, \sigma^{ii}) \exp\{-in(\omega_r t + \gamma)\} R_{spin}(t), \quad (ii = XX, YY, ZZ). \tag{150}$$

The coefficients $f^i_n(\alpha, \beta, \sigma^{ii})$ are related to the orientation of the molecule and to the CSA tensor elements. Following Tycko formalism,[77] let us write the following notation:

$$R_{spin}(t) I_Z = I_Z \cos\varepsilon + \frac{1}{2}\sin\varepsilon(I_+ e^{-i\zeta} + I_- e^{i\zeta}) \tag{151}$$

where $\varepsilon(t)$ and $\zeta(t)$ specify the direction of $R_{spin}(t)I_Z$ determined by the BABA pulse sequence. We investigated the particular case where $\varepsilon(t)$ is small, then $\cos\varepsilon(t) \to 1$, $\sin\varepsilon(t) \to 0$, and $R_{spin}(t)I_Z \approx I_Z$. For sake of simplicity, we rewrite the chemical shift coefficient as following:

$$\delta^i_{CSA}(t) = \sum_{n=-2}^{+2} f^i_n(\alpha, \beta, \sigma^{ii}) \exp\{-in(\omega_r t + \gamma)\}. \tag{152}$$

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

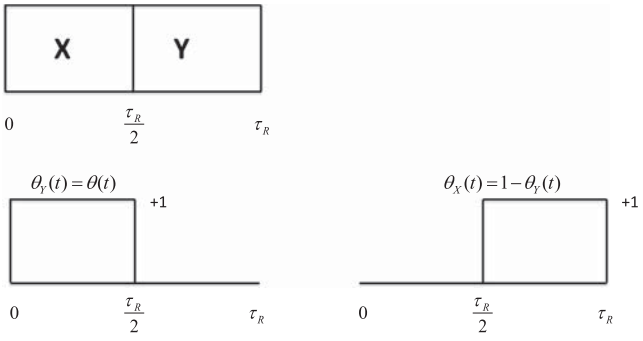
$$0 \le t \le \frac{t_R}{2}, \tag{153}$$

$$\begin{aligned} \widetilde{H}_{CSA}(t) &= \sum_i \delta^i_{CSA}(t) R^+_X(\frac{\pi}{2}) I^i_Z R_X(\frac{\pi}{2}) \\ &= \sum_i \delta^i_{CSA}(t) I^i_Y = H_Y \end{aligned} \tag{154}$$

and for $\frac{\tau_R}{2} \le t \le \tau_R$,

$$\begin{aligned} \widetilde{H}_{CSA}(t) &= \sum_i \delta^i_{CSA}(t) R^+_Y(\frac{\pi}{2}) I^i_Z R_Y(\frac{\pi}{2}) \\ &= -\sum_i \delta^i_{CSA}(t) I^i_X = H_X. \end{aligned} \tag{155}$$

Considering the BABA pulse sequence in the same picture as in reference[66]



The toggling frame is written as

$$\widetilde{H}_{CSA}(t) = H_Y(t)\theta(t) + H_X(t)(1 - \theta(t)) \tag{156}$$

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

$$\theta(t) = \sum_n a_n e^{-in\omega_R t} \tag{157}$$

where a_n represents the time-dependent Fourier coefficients corresponding to the Fourier index n. These

coefficients are described in the appendix. The toggling Hamiltonian can be written more explicitly as following

$$\widetilde{H}_{CSA}(t) = \sum_i (I_X^i + I_Y^i) \underbrace{\sum_{n=-2}^{+2} f_n^i a_{-n}}_{AHT = \bar{f}_n^{i(0)}} + \sum_i (I_X^i + I_Y^i) \sum_{m=-\infty}^{+\infty} e^{-im(\omega_R t+\gamma)} \underbrace{\sum_{n=-2}^{+2} f_n^i a_{m-n}}_{\bar{f}_n^{i(m)}} + \frac{1}{2} \sum_i \sum_{n=-2}^{+2} f_n^i(\alpha, \beta, \sigma^i) e^{-in(\omega_R t+\gamma)} (-I_X^i + I_Y^i). \tag{158}$$

The calculation of the first-order average Hamiltonian or the first-order contribution to the Floquet–Magnus expansion is given by

$$\begin{aligned} F_1 &= \frac{1}{T}\int_0^T \widetilde{H}_{CSA}(t)dt = \frac{1}{\tau_R}\int_0^{\tau_R} \widetilde{H}_{CSA}(t)dt \\ &= \sum_i \sum_{n=-2}^{+2} f_n^i a_{-n} (I_X^i + I_Y^i), \end{aligned} \tag{159}$$

which allows to obtain the following result:

$$F_1 = \sum_i (f_{-1}^i a_1 + f_0^i a_0 + f_1^i a_{-1})(I_X^i + I_Y^i) \tag{160}$$

or

$$F_1 = \sum_i \left[\frac{1}{\pi i}(f_1^i - f_{-1}^i) + \frac{1}{2} f_0^i\right](I_X^i + I_Y^i). \tag{161}$$

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

$$\frac{1}{\pi i}(f_1^i - f_{-1}^i) + \frac{1}{2} f_0^i = 0. \tag{162}$$

Similar analysis was also applied to dipolar interaction in the article.[66] The first order of the argument of the propagator operator in FME approach can be calculated as follows:

$$\Lambda_1(t) = \int_0^t \widetilde{H}_{CSA}(t')dt' - tF_1, \tag{163}$$

which gives the result:

$$\begin{aligned} \Lambda_1(t) = \frac{1}{2} \sum_i \sum_{n=-2}^{+2} f_n^i e^{-in\gamma^i} \left(\frac{-1}{in\,\omega_R}\right)(e^{-in\,\omega_R t} - 1) \\ \times (-I_X^i + I_Y^i) + \sum_i \sum_{m=-\infty}^{+\infty} \left(\frac{-1}{im\,\omega_R}\right)(e^{-im\,\omega_R t} - 1) e^{-im\gamma^i} \\ \times \sum_{n=-2}^{+2} f_n^i a_{m-n} (I_X^i + I_Y^i) \end{aligned} \tag{164}$$

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

$$\begin{aligned} \Lambda_1(t) = f_1\left(\frac{-1}{i\omega_R}\right)(e^{-i\omega_R t} - 1) I_Y + \frac{1}{2} f_{-1}\left(\frac{1}{i\omega_R}\right)(e^{i\omega_R t} - 1) \\ (-I_X + I_Y) \\ + f_2 \left[\frac{1}{2}\left(\frac{-1}{i2\omega_R}\right)(e^{-i2\omega_R t} - 1)(-I_X + I_Y) \right. \\ \left. + \frac{1}{\pi\omega_R}(e^{-i\omega_R t} - 1)\,(I_X + I_Y)\right] \\ + f_{-2}\left[\frac{1}{2}\left(\frac{1}{i2\omega_R}\right)(e^{i2\omega_R t} - 1)(-I_X + I_Y) \right. \\ \left. - \left(\frac{1}{3\pi\omega_R}\right)(e^{-i\omega_R t} - 1)(I_X + I_Y)\right] \end{aligned} \tag{165}$$

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

$$\begin{aligned} \frac{\Lambda_1(t)}{\tau_R} = f_1\left(\frac{-1}{4\pi i}\right)(e^{-i2\pi\varphi} - 1) I_Y + f_{-1}\left(\frac{1}{4\pi i}\right)(e^{i2\pi\varphi} - 1) \\ (-I_X + I_Y) \\ + f_2 \left[\left(\frac{1}{8\pi i}(e^{-i4\pi\varphi} - 1) + \frac{1}{2\pi^2}(e^{i2\pi\varphi} - 1)\right) I_X \right. \\ \left. + \left(\frac{1}{8\pi i}(e^{-i4\pi\varphi} - 1) + (e^{-i2\pi\varphi} - 1)\right)\left(\frac{1}{2\pi^2}\right) I_Y\right] \\ + f_{-2}\left[\left(\frac{-1}{8\pi i}(e^{i4\pi\varphi} - 1) - \frac{1}{6\pi^2}(e^{-i2\pi\varphi} - 1)\right) I_X \right. \\ \left. + \left(\frac{1}{8\pi i}(e^{i4\pi\varphi} - 1) - \frac{1}{6\pi^2}(e^{-i2\pi\varphi} - 1)\right) I_Y\right] \end{aligned} \tag{166}$$

where the variable is chosen to be a dimensionless number $\varphi = \frac{t}{\tau_R}$. We plotted the real, imaginary, and absolute parts of the function versus the dimensionless number to get information of the magnitude of the CSA in different orientation of the molecule. In this particular consideration, it appears that initially ($t = 0, \varphi \to 0$) and at one rotor period ($t = \tau_R, \varphi \to 1$), the magnitude of the CSA is null, which corresponds to $\frac{\Lambda(0)}{\tau_R} = \frac{\Lambda(\tau_R)}{\tau_R} = 0$. For $t = \frac{\tau_R}{2} \to \varphi = \frac{1}{2}$, we have

$$\begin{aligned} \frac{\Lambda_1(\frac{\tau_R}{2})}{\tau_R} = f_1\left(\frac{-1}{4\pi i}\right)(-2) I_Y + f_{-1}\left(\frac{1}{4\pi i}\right)(-2)(-I_X + I_Y) \\ + f_2\left[\frac{1}{2\pi^2}(-2) I_X + (-2)\left(\frac{1}{2\pi^2}\right) I_Y\right] \\ f_{-2}\left[\frac{-1}{6\pi^2}(-2) I_X - \frac{1}{6\pi^2}(-2) I_Y\right] \end{aligned} \tag{167}$$

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

$$\begin{aligned}\frac{\Lambda_1(\frac{\tau_R}{4})}{\tau_R} &= f_1(\frac{-1}{4\pi i})(-2)I_Y + f_{-1}(\frac{1}{4\pi i})(i-1)(-I_X+I_Y) \\ &+ f_2\Big[(\frac{1}{8\pi i}(-2) + \frac{1}{2\pi^2}(i-1))I_X \\ &+ (\frac{1}{8\pi i}(-2) + (\frac{1}{2\pi^2})(-i-1))I_Y\Big] \\ &+ f_{-2}\Big[(\frac{-1}{8\pi i}(-2) - \frac{1}{6\pi^2}(-i-1))I_X\ 0 \\ &+ (\frac{1}{8\pi i}(-2) - \frac{1}{6\pi^2}(-i-1))I_Y\Big] \end{aligned} \quad (168)$$

These instantaneous values of $\frac{\Lambda_1(t)}{\tau_R}$ mean 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.

5.3 *Advantages and limitations*

The goal of the FME in NMR is to bridge the AHT to the Floquet theorem but in a more succinct and efficient formalism.[18] Calculations can then be executed 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. This is due to the convergence issues when comparing the various theories used in NMR. Recent developments on the improvement of the bound for the convergence domain by Blanes *et al.*[167] and Casas *et al.*[166] reported that the bounds for the Fer, Magnus, and Floquet–Magnus expansions are$\xi_{FE} = 0.8604065$, $\xi_{Magnus} = 1.086869$, and $\xi_{FME} = 0.20925$, respectively. These results were obtained using a similar procedure and arguments. The rate of convergence of the FME is faster than the Fer and Magnus expansions in the sense that, for a prescribed precision, one needs both more Ω_k's (for the Magnus expansion) and F_k's (for the Fer expansion) than Λ_k's (for the Floquet–Magnus expansion); even if from the computational point of view, the Fer and Magnus expansions could require more work than the FME.

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 implementation of new or improvement of existing pulse sequence.

We expended the Floquet–Magnus expansion to the case of $\Lambda(0) \neq 0$. This gives the FME a new opportunity to construct the operator $\Lambda(t)$ to obtain the evolution of the system in between the stroboscopic detection points. The secular averaging theory (SAT) known as Floquet theory is a general approach developed more than a century ago for solving differential equations. Comparing the SAT and AHT results, a supplementary non-secular term appears in the second-order effective Hamiltonian, which is the main reason to invalidate the use of AHT in the interpretation of many NMR experiments.[81]

6. Potential approaches and future directions

All theories used in NMR rely on exponential Hamiltonian operator propagators. Therefore, computing the exponential of a matrix is a crucial task in quantum mechanics and NMR in particular. In the literature of numerical mathematics,[44,151,152] the approximation of the matrix exponential has a long history in its own right. Noteworthy are mathematical models of systems of linear, constant coefficient of ordinary differential equations, which describe many physical, biological, and economic processes. Although several powerful algorithms have been carried out in more systematic ways and show the vitality of the matrix exponential, efforts still need to be done to bring out some salient features not yet covered. As an example, the estimation of the function exp (C), where C is a (real or complex) N x N matrix, constitutes the main component in all parts of the computational penalty required by this category of algorithms and, as known, one of the most complicated characteristic. Moler and van Loan present in references[151,152] twenty distinct numerical algorithms for evaluating the exponential of a matrix. Methods such as Pade approximation, Chebyshev approximation, and Krylov space or splitting methods have been utilized to advance the understanding of the exponential matrix problem. In molecular quantum dynamics, simulation is essential particularly when dealing with chemical exchange or the restoration of equilibrium following disturbance where spectral lineshapes can be

imbricating. The major complication faced during simulation of spectra stems from the fast computational demands with an expanding number of spins. This is due to the expansion of the Hilbert space with the exponential scaling of the spin vector space. For instance, a state of n spin system is represented by 2^{2n}-dimensional vector. Therefore, the development of powerful numerical algorithms for dealing with cumbersome matrices that arise from complicated simulations is crucial. Numerical solution of the Liouville von Neumann equation or alternatively the numerical exponential of a Liouville matrix allows the simulation of spin system dynamics.[88]

In the next section, we present the Chebyshev approximation as a potential addition to the approaches described in this review. The Chebyshev approach has the prospective to expend its application in spin quantum including NMR. The enthusiasm of presenting the Chebyshev approach as a possible surrogate of the popular expansions in nuclear magnetic resonance for the assignment of numerical simulations in spin dynamics paradigm stems from its numerical steadiness and high precision. The theoretical lead of the Chebyshev method is still not utterly realized for present feasible computations.[88] Furthermore, in addition to the Chebyshev approximation, we are introducing another possible approach called Cayley transformation that could be assessed in some contexts.

6.1 *Chebyshev approach*

The past three decades witnessed the introduction of the Chebyshev approximation method of solving the time-dependent Schrodinger equation in the domain of molecular dynamics.[153–155] Tal-Ezer and co-workers proved that the superior approach to expand the evolution operator can be obtained by using the complex Chebyshev polynomials. Using the Chebyshev approximation, one can expand the evolution operator $\exp(-i\tau H)$ in a truncated series. Special mention should be given to a paper by Suli and Mayers[156] in which a useful function $F(x)$ in the interval [-1,1] is given and the Chebyshev polynomial approximations are most favourable in the sense that that the greatest error in the approach is reduced compared to most of the polynomial approximations. In particular, this method is used by connecting the extreme eigenvalues $E_{\min}$ and $E_{\max}$ of H. This allows the following inspection[44,157] of a reduced Chebyshev expansion of $\exp(-ix)$ on the interval $[\tau E_{\min}, \tau E_{\max}]$:

$$\exp(-ix) \approx \sum_{n=0}^{m} c_n P_n(x), \tag{169}$$

where

$$P_n(\tau) = T_n\left(\frac{2x - \tau E_{\max} - \tau E_{\min}}{\tau E_{\max} - \tau E_{\min}}\right) \tag{170}$$

with well-chosen coefficients c_n. One usually distinguishes two types of Chebyshev polynomials: $(T_n(x))$ and (U_n). The Chebyshev polynomials of the first kind, which are denoted, $T_n(x)$, on the interval $[-1, 1]$can be defined recursively as

$$T_{n+1}(x) = 2xT_n(x) - T_{n-1}(x); \tag{171}$$

$$T_1(x) = x; \tag{172}$$

$$T_0(x) = 1 \tag{173}$$

which gives the final approximation

$$\exp(-i\tau H) \approx \sum_{n=0}^{m} c_n P_n(\tau H). \tag{174}$$

Chebyshev polynomials are polynomials with the greatest possible dominant coefficient, but subject to the state where their complete value is bounded on the interval by 1. Using the Chebyshev method leads to major advantages such as utilizing the sparsity of the Hamiltonian by indicating the propagator in terms of a sequence of the Liouville superoperator (L) matrix multiples or the accuracy of the propagator of the Chebyshev expansion. The expansion converges very fast to the point where the truncation inaccuracy is smaller than the typical round-off errors succeptible to be present in most of the numerical calculation. Furthermore, the output expression in the expansion is close to the small number with the best performance for the exponential function represented by an orthogonal polynomial expansion.[88,155] The Chebyshev approach is regularly applied in numerical quantum dynamics to calculate $\exp(-i\tau H)\psi_0$ over very long times. One way of approaching this problem is to consider the m matrix-vector products with the above approximation used with a large truncation index m. The index m used to complete a particular precision is a linear function of the step size $\tau$and the spectral radius of H. The step size augmentation reduces the calculation work per unit step. In practice, m is chosen such that the round-off error governs the precision.[44,158,159] Although the Chebyshev approach presents several advantages and has been successfully applied to a number of problems, there are also existing drawbacks that need to be addressed. One such drawback concerns the unitary of the scheme. The Chebyshev method is not unitary and the norm is not conserved, but the difference with the unit is negligible due to the accuracy

of the technique. Another open drawback concerns the large time durations of propagation in the Chebyshev approach, which prevent intermediate results. To summarize, despite these drawbacks, we believe that the Chebyshev method will successfully serve the quantum spin dynamics community in establishing quantum mechanical time-dependent methods as a routine tool in quantum dynamics studies.

6.2 *Cayley method*

The Cayley transform is an alternative method to the exponential mapping relating the Lie algebra to the Lie group. The approach was developed more than a century ago by Cayley (1846) as a mapping between skew-symmetric matrices and special orthogonal matrices. The concept of relating the Lie algebra to the Lie group is particularly important for numerical methods where the calculation of the exponential matrix is the most difficult task of the algorithm.[44,174] Blanes and co-workers show that the solution of eq. (2) can be written as

$$U(t) = (I - \frac{1}{2}C(t))^{-1}(I + \frac{1}{2}C(t))U_0 \qquad (175)$$

with $C(t)$ obeying the so-called *dcayinv equation*[80,161]

$$\frac{dC}{dt} = -iH + i\frac{1}{2}[C, H] + i\frac{1}{4}CHC, \qquad (176)$$

$$t \geq t_0, C(t_0) = 0.$$

$-iH$ is element of the Lie algebra such that if B and C are also elements of a Lie algebra that can be combined by the Lie bracket, which we represent by $[H, B] = iC$, with the consideration of the orthogonal group, the Calyley transform can be written by

$$H = i(I - \alpha B)^{-1}(I + \alpha B). \qquad (177)$$

The choice of $\alpha = \frac{1}{2}$ is arbitrary but it ensures a particularly simple form of various expansion coefficients. Based on the above Cayley transform, Blanes et al. obtained the following time-symmetric methods of the orders 4 and 6.

Order 4:

$$C^{[4]} = \Omega^{[4]}(I - \frac{1}{12}(\Omega^{[4]})^2) = \alpha_1 - \frac{1}{12}[\alpha_1, \alpha_2] - \frac{1}{12}\alpha_1^3 + 0(h^5), \qquad (178)$$

where

$$C^{[4]} = C(h) + 0(h^5). \qquad (179)$$

Order 6:

$$C^{[6]} = \Omega^{[6]}(I - \frac{1}{12}(\Omega^6)^2(I - \frac{1}{10}(\Omega^{[6]})^2)) = C(h) + 0(h^7). \qquad (180)$$

For a total of nine matrix–matrix products per step, three matrix–matrix products are required in addition to the three commutators involved in the computation of $\Omega^{[6]}$. The articles[44,160,174] give the complete formulation of the scheme of $\Omega^{[6]}$. Manifestly, the Magnus-based integrators can generate efficiently the Cayley-based methods. However, truncated Caley expansions do not use some advantages related to the time symmetry. In the article,[160] Iserles demonstrated that the time symmetry is obtained when integrals are replaced by appropriate quadrature results. The Cayley method involves using explicit schemes for solving the differential equation on the Lie algebra of the group that leads to semi-implicit techniques where no recurrence is needed. The applications of the Cayley methods in the numerical solution of matrix differential systems on quadratic groups include but are not limited to the Penrose regression problem (PRP) where this approach has been used to obtain numerical solution of PRP,[161,163,164] the computation of Lyapunov exponents of Hamiltonian systems,[162,164] the solution of Hamiltonian isospectral problems,[161,164] etc.

7. Conclusion

In this article, we have thoroughly reviewed the abiding applications of the two main useful theories in NMR, the average Hamiltonian theory (Magnus expansion) and the Floquet theory from very different aspects of spin dynamics. We have also presented some applications and perspective of the developing and emerging theories in NMR (FE and FME). We have calculated the effective Hamiltonians of all these approaches. Effective Hamiltonians are important to understand how the pulse sequences work. We have presented results of Bloch–Siegert shift and CW decoupling for the AHT (Magnus expansion), Floquet theory, and Fer expansion to highlight the similarities and differences among these approaches. While the calculations involved in the Fer expansion are easier than in the Magnus expansion and Floquet theory, the later schemes give a clear perspective of the size of the correction associated with the order n.[188] Rather than being competitive, the AHT, the Floquet theory, the Fer expansion, and the Floquet–Magnus expansion can be considered as complementary. The level of success of each theory depends on the type of the physical problem to deal with. Combining two or more of the theories therein described could lead to a more general and unique framework for treating the time-dependent Hamiltonian in spin dynamics of NMR in a fashion that can be extended to synchronized and non-synchronized modulations.

We hope this review will encourage the use of Magnus and Fer expansions as numerical integrators. While we expect the use of Floquet–Magnus expansion as numerical integrator, we also encourage its use as an alternative approach in designing sophisticated pulse sequences, analyzing, and understanding of different experiments. Although the average Hamiltonian theory, the Floquet theory, and the developing theories such as the Fer expansion and the Floquet-Magnus expansion explain all aspects of spin dynamics in NMR, we insist on the fact that other perspectives and approaches beyond the scope of the current popular theories in the field of NMR need to be appraised.

Several phenomenal applications of the theories in NMR have not been discussed in this review paper. One which has shown itself very useful was the multiple quantum NMR dynamics. Special recommendation should be made for the new field of quantum information processing and computing in which NMR quantum calculations of the Jones Polynomial is performed.

Although the theories in NMR, such as those considered here, in principle, to solve time-dependent Schrodinger equation, there are still several problems that have not been explored in the field of NMR. A general theoretical description of NMR experiments assists many time-dependent perturbations with incommensurate frequencies. However, formalized theoretical approaches such as "operator-based Floquet" do not present a theoretical treatment of problems beyond four incommensurate frequencies. With the multiplication of the degree of refinement of NMR experiments, higher-order expressions are of expending importance, such as in diffusion experiments. We believe that the domain of applications of Floquet–Magnus expansion and Fer expansion will also widen over the years. We also expect the FME to generate new contribution like the generation of efficient numerical algorithm for geometric integrators. We hope that this overview of the theories and applications in NMR spectroscopy will continue to strenghten interactions between NMR spectroscopists and other specialists such as in Mathematics, Physics, Chemistry, and Chemical Physics.

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Conflict of Interest

The author confirms that this review content has no conflict of interest.

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