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Investigation of timing effects in modified composite quadrupolar echo pulse sequences by mean of average Hamiltonian theory

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ABSTRACT

The utility of the average Hamiltonian theory and its antecedent the Magnus expansion is presented. We assessed the concept of convergence of the Magnus expansion in quadrupolar spectroscopy of spin-1 via the square of the magnitude of the average Hamiltonian. We investigated this approach for two specific modified composite pulse sequences: **COM-Im** and **COM-IVm**. It is demonstrated that the size of the square of the magnitude of zero order average Hamiltonian obtained on the appropriated basis is a viable approach to study the convergence of the Magnus expansion. The approach turns to be efficient in studying pulse sequences in general and can be very useful to investigate coherent averaging in the development of high resolution NMR technique in solids. This approach allows comparing theoretically the two modified composite pulse sequences **COM-Im** and **COM-IVm**. We also compare theoretically the current modified composite sequences (**COM-Im** and **COM-IVm**) to the recently published modified composite pulse sequences (**MCOM-I**, **MCOM-IV**, **MCOM-I_d**, **MCOM-IV_d**).

1. Introduction

Until recently, very little was known about the convergence of the exponential perturbation theory. The formulation of the convergence of the average Hamiltonian theory (AHT) and its antecedent the Magnus expansion had attracted much attention over the last half a century [1–16]. Magnus's convergence criterion in his original version of the expansion is expressed in function of the eigenvalues of the exponent itself [14]. Recent progress has been made by performing calculations on NMR and physical interesting model systems [7,17–25] to improve the understanding of the convergence of the exponential perturbation theory. The method we presented in this paper show that the magnitude of the average Hamiltonian can also be useful in the Schrodinger representation. This approach include also a number of models such as those used in scattering, dynamics, and problems of perturbation involving adiabatic approximation, atomic and molecular systems. While this approach of convergence is very useful in many situations, it is important to mention that in some cases such as an infinite series, convergence has nothing to do with the magnitude of the initial certain number of terms. One only needs to look at the magnitude of the terms omitting the first few terms. In this paper, we associated the process of evolution of spin dynamics under a periodic Hamiltonian $H(t)$ to the problem of convergence. In general, the convergence is view as the act of coming together of different and separate phenomenon. This notion is very used in quantum physics, especially in the control of spin dynamics that is helpful to understand the spin experiments fidelity. A typical milestone physical example of convergence is the celebrate spin echo which is the refocusing of an NMR signal due to dephasing of the nuclear spins [17,18]. Milestone theories in solid state NMR such as AHT and Floquet theory have been used for creating contrived interactions [26–32].

This manuscript compares modified composite pulse schemes by estimating the square of the zeroth-order in the AHT expansion of the quadrupolar Hamiltonian under the modified composite sequences. The paper presents the applicability of the AHT as intimately related to the convergence of the Magnus expansion which was extensively discussed by Maricq [5–7], Fel'dman [8,32–34], Salzman [9–12] and others [13]. It is important to outline that the Magnus ‘convergence has played a crucial role in the field of NMR and we exploited this aspect in this work. It is also important to outline that, in the early days of the investigation of the

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convergence of the Magnus expansion for spin systems in periodic magnetic fields, conflicting opinions have appeared in the literature to validate the average Hamiltonian approach [8]. Fortunately, Fel'dman has provided an illuminating article [8] that clarified the mathematical point of view of the convergence of the Magnus expansion. Our analysis focused on the convergence of the AHT based on the Magnus expansion which was shown to not always be convergent such as in spin systems of periodic magnetic fields [8]. The analysis of the convergence of the square of the Magnus expansion enables us to elucidate the quadrupolar spectroscopy for spin-1 when irradiate with composite sequences. We assumed that the square of the Magnus expansion is valid within the framework of the original Magnus expansion. Experimental results were recently presented in Ref. [47]. These results show an optimum excitation realized by using COM-IVm compared to COM-Im. The coverage of the excitation profile resulting from COM-IVm is twice as large as that resulting from a single pulse. The two modified composite sequences, **COM-Im** and **COM-IVm** are selected due to their less and best excitation profile, respectively, among the composites sequences investigated in Ref. [35]. We mainly study the square of the magnitude of the AHT in order to theoretically compare two modified composite pulse sequences (**COM-Im** and **COM-IVm**) and describe the behavior of quadrupolar spin systems subject to these modified composite quadrupolar echo pulse sequence irradiation. We compare theoretically, the current modified composite sequences (**COM-Im** and **COM-IVm**) to the recently published modified composite pulse sequences (**MCOM-I**, **MCOM-IV**, **MCOM-I_d**, **MCOM-IV_d**) [36,37]. The current modified composite pulse sequences (**COM-Im** and **COM-IVm**) studied in this paper differs from those recently investigated in Refs. [36,37] by the time sequence associated to each composite sequence, especially during the free evolution time intervals. We assume that the size of the square of the magnitude of zero order average Hamiltonian obtained on the appropriated basis is a viable approach to study the convergence of the Magnus expansion. This approach turns to be efficient in comparing pulse sequences and can be used in other cases such as coherent averaging in NMR, the development of the high-resolution NMR technique in solids as well as for the interpretation of a number of fine NMR experiments in solids. Composite pulse sequences are very important for the general field of spin dynamics and were introduced to the field of NMR by Levitt and Freedman [38] nearly four decades ago. A composite pulse is a cluster of several square pulses whose lengths or flip angles and phases are chosen to correct for the pulse imperfections and overcome the negative effects during spin dynamics. This technique has played a major role and has been widely used in the field of magnetic resonance [38,39] and in quantum computing.

In the following section 2 of the paper, we present the theoretical background of the Euclidian norm to express the magnitude of the square of $\left\|\overline{H}^{(n)}\right\|$. In section 3, we present the calculations of AHT applied to quadrupolar spin system (I = 1) when irradiated with the modified composite echo pulse sequences (**COM-Im**, **COM-IVm**, **MCOM-I**, **MCOM-IV**, **COM-I_d**, and **COM-IV_d**). Section 4 and are devoted to the results and the numerical data, respectively. In section 5, we discuss the theoretical results obtained based on the convergence of the Magnus expansion. Section 6 concludes the article.

2. Theory

2.1. Mathematical analysis

Let us define the square of the sum of coefficients of the various spin operators who are the generators for the Hamiltonians $H(t)$. The analysis proceeds by a series expansion of $H(t)$,

$$H(t) = H^{0}(t) + H^{(1)}(t) + H^{(2)}(t) + \dots. \tag{1}$$

It is known that a series $H(t)$ is convergent if the sequence of its partial sums converges, or in other words it approaches a given number. There exists a limit l such that for any arbitrary small positive number $\varepsilon > 0$, there is a large integer N such that for all $n \geq N$,

$$|H(t) - l| \leq \varepsilon. \tag{2}$$

Let the spin operators $I_{p,1}$, $I_{p,2}$, and $I_{p,3}$ be the generators for the Hamiltonian H, where

$$I_{p,1} = \frac{1}{2} I_p \tag{3}$$

$$I_{p,2} = \frac{1}{2}\left(I_q I_r + I_r I_q\right) \tag{4}$$

$$I_{p,3} = \frac{1}{2}\left(I_r^2 - I_q^2\right) \tag{5}$$

with $p = x, y, z$ and $(p, q, r) = (x, y, z)$, the cyclic permutations. The nth order average Hamiltonian, $\overline{H}^{(n)}$, can be written in term of the fictitious spin-1 operator formalism of Vega and Pines [41] defined by the operators $\{I_{p,1}, I_{p,2}, I_{p,3}\}$ such as

$$\overline{H}^{(n)} = Span\{I_{p,1}, I_{,p,2} I_{p,3}\} \tag{6}$$

with $n = 0, 1, 2, 3 \ldots\ldots$

The set of operators, $\{I_{p,1}, I_{p,2}, I_{p,3}\}$ constitutes the generators of $\overline{H}^{(n)}$. For instance, we have

$$\overline{H}^{(0)} = Span\{I_{p,1}, I_{,p,2} I_{p,3}\}, \tag{7}$$

$$\overline{H}^{(1)} = Span\{I_{p,1}, I_{,p,2} I_{p,3}\}, \tag{8}$$

$$\overline{H}^{(2)} = Span\{I_{p,1}, I_{,p,2} I_{p,3}\}, \quad \cdots \quad \cdots \tag{9}$$

$$\overline{H}^{(n)} = Span\{I_{p,1}, I_{,p,2} I_{p,3}\}. \tag{10}$$

The basis of the fictitious spin-1 operators of the nth order average Hamiltonian ($\overline{H}^{(n)}$) over the Magnus expansion is a linearly independent subset of $\overline{H}^{(n)}$. For the spanning property, we can explicitly, write that

$$\overline{H}^{(n)} = a_{p,1} I_{p,1} + a_{p,2} I_{p,2} + a_{p,3} I_{p,3}, \tag{11}$$

where the numbers $a_{p,1}, a_{p,2}, a_{p,3}$ are called the coordinates of the nth order average Hamiltonian, $\overline{H}^{(n)}$, with respect to the fictitious spin-1 operator basis $\{I_{p,i}\}, i = 1, 2, 3$. These coordinates are uniquely determined. The basis $\{I_{p,i}\}$ is finite-dimensional. To handle infinite-dimensional spaces, we must generalize the finite basis sets to include infinite basis sets. In this study, $\overline{H}^{(n)}$, is associate to a vector, hence has a basis. All order of the average Hamiltonian ($\overline{H} = \overline{H}^{(0)} + \overline{H}^{(1)} + \overline{H}^{(2)} + \ldots$) can be associated to a vector with a basis. Every order of the average Hamiltonian (i.e. vector) can be expressed as a linear combination of the fictitious spin-1 operators' basis in a unique way. If the basis is ordered, then the coefficients in this linear combination yield coordinates of the n-order of the average Hamiltonian ($\overline{H}^{(n)}$) relative to the basis. For many reasons, it is opportune to deal with an ordered basis. For instance, when working with a coordinate representation of a vector, it is usual to speak of the first or second coordinate, which makes sense only if an ordering is specified for the basis. An ordered basis is also called a frame.

In this work, we make use of an important notion of linear algebra and functional analysis called "normed vector space". It is more common to