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Progress in spin dynamics solid-state nuclear magnetic resonance with the application of Floquet–Magnus expansion to chemical shift anisotropy

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ABSTRACT

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

1. Introduction

Soon after finishing his graduate studies, Erwin Hahn burst on the world of science with his remarkable observation of spin echoes. This discovery provided key impetus to the development of pulse methods in nuclear magnetic resonance (NMR), and must therefore be ranked among the most significant contributions to magnetic resonance [1]. Since the discovery of spin echoes in 1950 by Hahn [2], all manipulations of spins and spin interaction by radio-frequency or microwave pulses have been accurately described by quantum mechanics and mathematics that lend to creativity and new insights. Nowadays, the technique of NMR is a vibrant and central area of research, with contributions from scientists in nearly all fields of physical, chemical, biological sciences, and mathematics. Though there are multiple levels of complexity, the technique of magnetic resonance has been made simple to the end user: a sample of interest is placed in a strong magnetic field, followed by the application of radio-frequency or microwave pulses, and the resulting signal emitted by the sample is detected [3–5].

Various theories have been developed and introduced over time in magnetic resonance to predict, describe or control coherently the dynamics governing spin systems. These theories include but are not limited to Floquet theory (FLT) [6,7], average Hamiltonian theory (AHT) [8,9], Floquet–Magnus expansion (FME) [6,8,10], and Fer expansion (FE) [11,12]. The paper is organized as follows: the next section summarizes the essential background information about the FLT, AHT, FME, and FE. The first application of the FME to the chemical shift anisotropy (CSA) when irradiated with the BABA pulse sequence is presented in the Section 2.4. Finally, Section 3 of the paper discuss and summarizes our conclusions.

2. Various theories in solid-state nuclear magnetic

2.1. Resonance

Numerous approaches have been used in solid-state NMR. Out of these approaches, only AHT and FLT have been widely utilized, whereas the Fer and Floquet–Magnus expansions were introduced very recently to NMR. The AHT is a perturbative approach while the FLT is a more general approach than AHT. The Floquet theory approach has been a powerful method for describing the full time dependence of the response of a periodically time-dependent system. The FLT method provides a framework for treating time-dependent Hamiltonians in NMR in a way that can easily be extended to several non-synchronized modulations [13–16]. For instance, it can be applied to time-dependent quantum systems exploiting the propagator for a periodic Hamiltonian that lead to a time-independent Hamiltonian. Under such circumstances of the

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time-independent Floquet–Hamiltonian approach, the time-dependent Hilbert-space Hamiltonian is transformed into an infinite-dimensional Hilbert space [7,17,18]. For numerical computations, the infinite dimension of the Hilbert space has to be truncated. Matrix representations are usually used when the FLT is applied to spectroscopy [13,20,22]. The value and applicability of this approach lead Shirley [7] in 1965 to introduce this scheme to spectroscopy to solve the periodically time-dependent Schrodinger equation. From this initial introduction of FLT to quantum physics, the field of nuclear magnetic resonance spectroscopy has gained momentum with a continuous stream of conceptual advances and methodological innovations with new applications continuously increasing [19–24]. The two milestones theoretical approaches (AHT, FLT) and the two newly introduced theoretical approaches (FE, FME) used for NMR include.

2.1.1. Average Hamiltonian theory

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

$$\overline{H}_0 = \overline{H}_0^{(0)} + \overline{H}_0^1 + \overline{H}_0^2 + \cdots \tag{1}$$

with

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

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

where $\tilde{H}_0(t)$ is the toggling frame Hamiltonian. The toggling frame Hamiltonian is the Hamiltonian in the time-dependent interaction representation with respect to the perturbed Hamiltonian. The central result of AHT (Eq. (1)) is obtained by expressing the evolution propagator $U(t_c)$ (given in Section 3) by an average Hamiltonian $\overline{H}_0$ and using the Magnus expansion [62] which forms the basis of AHT.

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

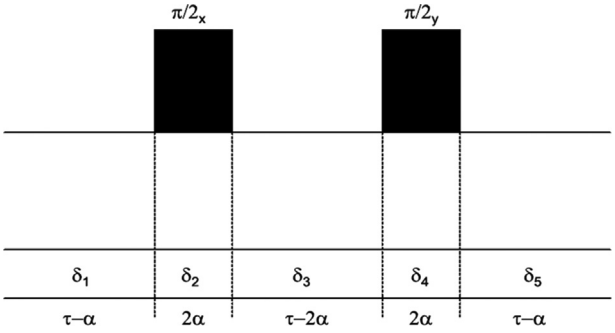

Fig. 1. Solid echo pulse sequence for refocusing the quadrupolar Hamiltonian. The two $\pi/2$ phase. shifted pulses are separated by a delay τ-2α, where 2α is the $\pi/2$pulse width. The phases (x,y) of the two-pulses shown can be any combination of phase shifted 90 degree pulses.

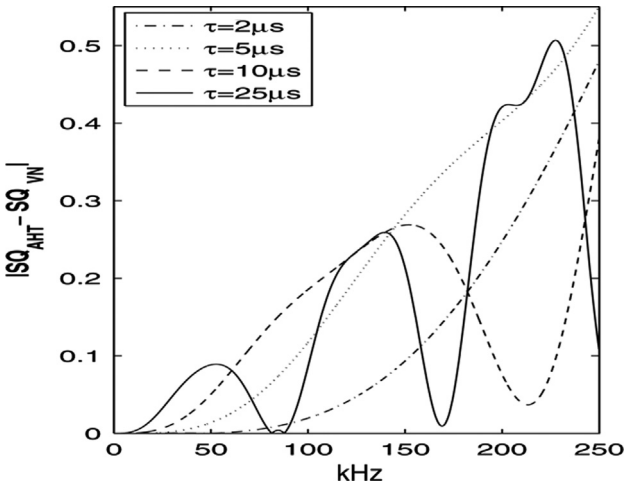

Fig. 2. Absolute value of the difference of the observable single quantum (SQ) coherences for spin $I=1$ as predicted by first-order AHT and that from a numerical solution to the VN equation for the pulse sequence shown in Fig. 1 for different values of τ.