Solid State Nuclear Magnetic Resonance 53 (2013) 20–26

Contents lists available at SciVerse ScienceDirect

Solid State Nuclear Magnetic Resonance

journal homepage: www.elsevier.com/locate/ssnmr

Complete description of the interactions of a quadrupolar nucleus with a radiofrequency field. Implications for data fitting

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ARTICLE INFO

Article history:
Received 7 January 2013
Received in revised form
9 February 2013
Available online 4 April 2013

Keywords:
Radiofrequency fields
Nutation
Flip angles
Quadrupolar nuclei
Liouvillians
Data fitting

ABSTRACT

We present a theory, with experimental tests, that treats exactly the effect of radiofrequency (RF) fields on quadrupolar nuclei, yet retains the symbolic expressions as much as possible. This provides a mathematical model of these interactions that can be easily connected to state-of-the-art optimization methods, so that chemically-important parameters can be extracted from fits to experimental data. Nuclei with spins $>1/2$ typically experience a Zeeman interaction with the (possibly anisotropic) local static field, a quadrupole interaction and are manipulated with RF fields. Since RF fields are limited by hardware, they seldom dominate the other interactions of these nuclei and so the spectra show unusual dependence on the pulse width used. The theory is tested with ^{23}Na NMR nutation spectra of a single crystal of sodium nitrate, in which the RF is comparable with the quadrupole coupling and is not necessarily on resonance with any of the transitions. Both the intensity and phase of all three transitions are followed as a function of flip angle. This provides a more rigorous trial than a powder sample where many of the details are averaged out. The formalism is based on a symbolic approach which encompasses all the published results, yet is easily implemented numerically, since no explicit spin operators or their commutators are needed. The classic perturbation results are also easily derived. There are no restrictions or assumptions on the spin of the nucleus or the relative sizes of the interactions, so the results are completely general, going beyond the standard first-order treatments in the literature.

1. Introduction

Radiofrequency (RF) irradiation is the main tool we use to manipulate and observe spin dynamics in nuclear magnetic resonance (NMR). Combined with free precession during delays, RF pulses are assembled into pulse sequences that can perform what seems to be spectroscopic magic. For simple systems, such as those with spins-1/2, the design and analysis of these pulse sequences is well understood, but for quadrupolar nuclei, the situation is usually more complex. If the RF dominates all the other interactions of the nucleus, then a pulse is effectively instantaneous and acts like a rotation of the frame of reference. For quadrupolar nuclei, the interactions are large and the RF almost never dominates. In the time domain, this means the spin system is evolving under both the static Hamiltonian and the RF, so more than one transition is being affected at the same time. Even though we talk about a π pulse, this may not have the same effect as rotating the frame of reference through that angle. Finite pulse effects are becoming more common in NMR and so a deep understanding of the effect of RF is essential. Such an important aspect of NMR has been widely studied in the literature, of course, but often with some simplifying assumptions. This paper includes and extends existing work and presents a simple yet complete and exact approach to the effects of RF on a single static quadrupolar nucleus of arbitrary spin. No assumptions, such as first-order coupling or on-resonance irradiation are required. The theory is subjected to the most rigorous testing: nutation behavior of all the ^{23}Na transitions of a single crystal of sodium nitrate.

It is useful to divide the NMR of quadrupolar nuclei into two classes: first-order perturbed and second (or higher) order perturbed. The first-order case is easy to deal with, but the spectra contain little information, since the central transitions all have the same frequency regardless of orientation. Second-order perturbed systems are more common (since quadrupole couplings tend to be large and there are limits to magnetic field), and the powder pattern of the central transition shows a rich structure. Essentially all of the published analysis of RF effects is restricted to first-order systems. However, the theory is not restricted to this simple case, and it reveals a number of complications that arise in higher-order systems. These are observed experimentally in the often-unusual flip-angle dependence of second-order spectra. In this paper we establish and test the method, and future work will give details of the effects of strong quadrupolar coupling.

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0926-2040/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.ssnmr.2013.03.002

We usually want to extract molecular parameters from experimental spectra. It is important to remember that the mathematical model is a means to an end in this process. The parameters in the model are usually varied systematically until a best fit to the data is obtained. This is an optimization problem [1] which can be handled in a number of ways. Roughly, such problems divide into cases where derivatives are available or where they are not. Derivative-based methods tend to be more efficient, but they can be difficult to implement and numerically expensive. In this paper, we discuss both methods for the nutation experiment and show how symbolic derivatives can be easily calculated within this approach. A numerical simulation will give numerical derivatives, which are typically less reliable. Furthermore, people typically fit a single spectrum to a model based on the equilibrium state [2]. If we can broaden this to a set of spectra as a function of a readily-controlled experimental parameter, such as flip angle, then we will get better data.

The spin dynamics of a quadrupolar nucleus subjected to the Zeeman interaction (which includes chemical shielding anisotropy) and quadrupolar coupling is well-known [3–7], but the full interaction with a radiofrequency (RF) field, combined with the others, is less so [8–38]. In the quest for simple analytical formulae, many of these studies used simplifying, but well justified assumptions, such as first-order coupling, on-resonance irradiation or cylindrical tensors. Most of this published work assumes the quadrupole Hamiltonian is proportional to I_z^2, which is equivalent to first-order perturbation. As well, it is often (with some exceptions [28]) assumed that the RF is on-resonance with the central transition—this would prevent us from analyzing powders with a CSA contribution. There is also the question of whether the dependence on pulse width should be Fourier transformed to give a nutation spectrum, or just left as a flip-angle dependence of the normal spectrum. Finally, most samples are powders, so a powder average is then superimposed on the nutation behavior. This is appropriate for real samples, but it will average out many of the details. A single crystal study is a much more challenging experimental test of the theory.

In this paper, we present a unified theory which treats all of these interactions which follows on a preliminary communication [36]. The specific results can be derived by a number of other techniques, including a very recent analysis using effective Hamiltonians [37], so the stress here is on the method and its experimental test. Finally, we use optimization methods to fit the theory to experiments and start a discussion of the calculation of derivatives of the results with respect to the parameters—a necessary next step in fitting procedures.

The theory is exact and completely general, with no restrictions on the relative sizes of the RF, Zeeman and quadrupole interactions and it has proved useful in the case of third-order perturbations to the central transition [39]. Explicit formulae for the results can not be derived for the general case, but symbolic solutions are available for simple cases [40]. The goal is not to derive a series of formulae, rather it is to formulate it in terms of an eigenvalue problem. There are explicit formulae for the matrix elements, so that all that is needed is an eigenvalue (symbolic or numerical) routine, such as those available in higher-level programs such as Matlab (http://www.mathworks.com), Mathematica (http://www.wolfram.com) or Maple (http://www.maplesoft.com). If the program handles symbolic manipulation (e.g. Mathematica or Maple), then even the formulae can be easily generated by the program, for added reliability. In this way, there are no special cases—since the parameters are general, any case can be handled by the same program. There is a very close analogy between this approach and the way we deal with Hamiltonians: in both cases, there is a basis denoted by spin quantum numbers and a set of formulae for the matrix elements. The original source of the formulae may be daunting, but their use is very straightforward. This provides an easy and accessible way to calculate the full spin dynamics for a general quadrupolar spin.

2. RF pulse effects

The effects of RF irradiation are well-known for spin-1/2 nuclei. If the RF dominates all interactions, the effects are equivalent to the rotation of the frame of reference. Even if the RF is off-resonance, then it still acts as a rotation, albeit around a tilted effective axis [4,41–43]. For quadrupolar nuclei, the RF can affect the central transition and the satellites simultaneously, so the situation is more complicated. If the RF dominates the quadrupole interaction, then the behavior is like a spin-1/2. If the quadrupole dominates the RF, then the RF usually affects only a single transition, which can be treated as a fictitious spin-1/2. The most complicated case is a powder pattern for a system with a strong quadrupole. In this case, the central transition is shifted by the second-order quadrupole perturbation, which depends on orientation and can give substantial width to the central transition lineshape. In practice, this is often the case encountered, and leads to substantial flip-angle dependence of the powder lineshape. Within the powder, there will be orientations where the RF dominates and those where the quadrupole dominates and all the in-between cases, so a general approach is essential. Describing this is our ultimate goal.

Since NMR is such a simple quantum-mechanical system, these problems can already be treated fully with a number of approaches. They all must give the same answer, but various people may find particular approaches more useful, so it is important to have alternatives. Numerical integration of the equation of motion of the density matrix is readily available with modern computers and software, such as SIMPSON [44], SPINEVOLUTION [45] or SpinDynamica (http://www.spindynamica.soton.ac.uk) to give an exact solution, but this may not give much physical insight and may be numerically inefficient because of different time scales. Also, the output may not be in a convenient format for further processing. For smaller spin systems, particularly spin-3/2, reasonable approximations can be made and symbolic expressions can be derived. We always start with a symbolic statement of the problem and end up with numerical values to compare with experiments. The question arises as to when to make this transition. If there is a full symbolic solution (*e.g.* from perturbation theory), then there are no numerical issues. A fully numerical solution is a good general way to proceed, but there may be questions about step sizes and round-off errors. This situation is amplified if we try to calculate derivatives purely numerically. If we start with a partly symbolic approach, then this may focus the numerical issues in one step (perhaps an eigenvalue routine) where the numerical issues are well-studied. There is no "best" way, since any numerical method has flaws. The approach we present here tries to maintain as much of the symbolic solution as possible, but also provides an easy route for exact numerical simulation.

A challenging test for these theories is the spin nutation experiment. For an isolated spin-1/2, the plot of signal against pulse width will be a sine wave, and has often been used for calibrations of the RF field. For a quadrupolar system, the plot is a sum of sine waves whose frequencies and intensities depend on the relative sizes of the quadrupole interaction and the RF field [8,11–13,16,26,28,29,31,36,37,46–49]. A related situation is the direct creation of multiple-quantum coherence during a finite pulse [50–52]. In all these cases, the Zeeman, the quadrupole and the RF interactions must be treated together, with no assumptions of their relative magnitudes.