

Communication

A simple proof that third-order quadrupole perturbations of the NMR central transition of half-integral spin nuclei are zero

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Received 13 December 2005; revised 10 January 2006

Available online 25 January 2006

Abstract

It has been known for a long time that the third-order quadrupole corrections to transitions from $m_z = -n/2$ to $m_z = +n/2$ are zero in the NMR of half-integer nuclei. However, the derivation has relied on deriving the corrections to the energy levels through somewhat laborious calculations. Only when the transitions between the levels were calculated was it revealed that the corrections to the transition frequency were zero. In this paper, we use Liouville-space methods to work with the transitions directly. Application of a recently published [A.D. Bain, Exact calculation, using angular momentum, of combined Zeeman and quadrupolar interactions in NMR, *Mol. Phys.* 101 (2003) 3163–3175] selection rule for the quadrupole coupling leads to a very simple proof that third-order corrections to the central and other symmetrical transitions are zero. The simplicity of the proof suggests there is a fundamental symmetry involved.
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Keywords: Quadrupolar nuclei; Perturbation theory; Second-order effects; Third-order effects; Solid-state NMR

Many of the nuclei in the periodic table are quadrupolar, i.e., they have a spin greater than 1/2 [1–5]. This means that the different orientations of the nuclear spin can interact with the field gradient at the nucleus generated by the electrons in the molecule. When the nucleus is in a magnetic field, there are then two competing influences: the Zeeman interaction with the (lab-based) magnetic field and the quadrupole interaction with the (molecule-based) electric field gradient. In many cases, the quadrupole interaction is small enough that it can be treated with perturbation theory. However, systems with larger and larger quadrupole couplings are now being studied [6–13].

For half-integral nuclei, the first-order correction to the so-called central transition (from $-1/2$ to $+1/2$) is zero, and there are commonly used algebraic formulae for the second-order correction [14]. Higher-order corrections to the wavefunctions have been published [14–19], as have a number of exact solutions [10,20–25]. In practice, we find that

second-order perturbation theory works remarkably well. In this paper, we show that the third-order correction to the position of the central transition is exactly zero, which partly explains this observation. This is a well-known result in the literature [10,11,18,19], but we present a new, clear, and simple derivation.

This result is based on a recently published selection rule [25]. The calculation uses the principle that the NMR transitions can be calculated directly, by setting up and diagonalizing the Liouvillian [26]. The Liouvillian is the commutator with the Hamiltonian, and its matrix representation is calculated in an operator basis. If a spherical tensor operator basis is used, then each basis operator has an angular momentum associated with it, corresponding to the rank and the order of the spherical tensor. The angular momentum has one quantum number giving the total angular momentum and another which gives the z component. We have dubbed this angular momentum “superspin” [27]. We showed [25] that the Liouvillian matrix element of the quadrupole interaction is zero unless the superspins of the two basis operators differed by exactly 1. This allowed us to solve for the transitions for any strength

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of the quadrupolar interaction, and to observe these transitions experimentally [28]. The results showed that second-order perturbation theory was remarkably good, which has led us to look at higher-order terms.

There is a theorem in quantum mechanics [29] that knowledge of the wavefunction to order n will give the energy to order $(2n + 1)$. In our case, we work directly with the transitions, but the mathematics is identical. Since standard formulae for quadrupole-perturbed NMR spectra give the operator nature of the transitions to first order [30], the third-order corrections to the transition frequencies are readily calculated.

Let \mathcal{Q} be the quadrupole perturbation. The superspin basis operators are eigenfunctions of the Zeeman interaction [25], which is the unperturbed Liouvillian in this case. We suppress the z component of superspin, and denote a basis operator with total superspin N as a Liouville-space ket $|N\rangle$ [27]. Let $\psi_k^{(0)}$ be the unperturbed transition and let $\psi_k^{(1)}$ be the small first-order correction to the transition. The unperturbed frequency, $\nu_k^{(0)}$ and its first, second, and third-order corrections [29] (the order is given in the superscript) are given by Eq. (1):

$$\begin{aligned} \nu_k^{(1)} &= \left(\psi_k^{(0)} | \mathcal{Q} | \psi_k^{(0)} \right), \\ \nu_k^{(2)} &= \left(\psi_k^{(0)} | \mathcal{Q} | \psi_k^{(1)} \right), \\ \nu_k^{(3)} &= \left(\psi_k^{(1)} | \mathcal{Q} | \psi_k^{(1)} \right) - \nu_k^{(1)} \left(\psi_k^{(1)} | \psi_k^{(1)} \right). \end{aligned} \quad (1)$$

Similarly, the first-order correction to the transition can be written as an expansion in terms of the eigenfunctions of the unperturbed Liouvillian. The first-order correction to transition $\psi_k^{(1)}$ is given by Eq. (2)

$$\psi_k^{(1)} = \sum_N \frac{(N | \mathcal{Q} | \psi_k^{(0)})}{\nu_k^{(0)} - \nu_N^{(0)}} |N\rangle. \quad (2)$$

Before we start the full calculation, note that for the central transition, the second term in the third-order correction is zero, since $\nu_k^{(1)} = 0$. The central transition is unperturbed to first order by the quadrupole interaction.

Any perturbation calculation is based on the eigenfunctions of the unperturbed Liouvillian, which in this case is the Zeeman interaction. These are the superspin kets, so $\psi_k^{(0)}$ has a definite value of its total angular momentum.

To calculate the third-order correction, we substitute Eq. (2) into the third equation in (1). We are concentrating on the central transition, so the second term in (1) will be dropped

$$\begin{aligned} \nu_k^{(3)} &= \left(\psi_k^{(1)} | \mathcal{Q} | \psi_k^{(1)} \right) \\ &= \sum_M \sum_N \frac{(M | \mathcal{Q} | \psi_k^{(0)})}{\nu_k^{(0)} - \nu_M^{(0)}} \frac{(N | \mathcal{Q} | \psi_k^{(0)})}{\nu_k^{(0)} - \nu_N^{(0)}} (M | \mathcal{Q} | N). \end{aligned} \quad (3)$$

In order for the matrix element $(M | \mathcal{Q} | N)$ to be non-zero, M and N must differ by exactly one unit, due to the selection rule. If N and $\psi_k^{(0)}$ also differ by one unit, then it is impossible for M and $\psi_k^{(0)}$ to do so. One of the three matrix

elements must be zero. Therefore, the expression in Eq. (3) must vanish. This means that for the central transition, both terms in the third-order correction will be zero. The same argument will apply to all multiple-quantum transitions from $m_z = -n/2$ to $m_z = +n/2$. For the single-quantum satellites, the first term in Eq. (2) will be zero, but the second will usually be finite and directly proportional to the quadrupole coupling (the first-order term).

This simple derivation indicates a fundamental symmetry in the quadrupole interaction, which is tied to the angular momentum properties of the system. We are pursuing further consequences of this symmetry.

Acknowledgments

I thank Dr. Paul Ayers, Dr. Giuseppe Melacini, and Dr. Gillian Goward for helpful discussions. Funding for this work was provided by the Natural Sciences and Engineering Research Council of Canada (NSERC).

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