

Quadrupolar Nuclei in Liouville Space

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INTRODUCTION

We know that quadrupolar nuclei have a molecule-fixed interaction with the electric field gradient which competes with the lab-fixed Zeeman interaction. For half-integral nuclei, the quadrupole interaction does not affect the central transition (from $-1/2$ to $+1/2$) to first order. The second-order terms are not zero (7), and lead to typical powder patterns when the quadrupole coupling is substantial (figure 1). Higher-order corrections to the wavefunctions have been published (7-6), as have a number of exact solutions (7-74).

In practice, we find that second-order perturbation theory works remarkably well. This is partly because the third-order correction to the central transition is exactly zero (5,6,13,15). This result is not new, but this poster is about a simple method of deriving it (16), using Liouville-space methods.

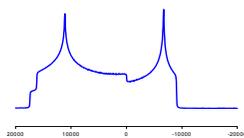


Figure 1

HAMILTONIAN METHODS

Basis Set

For a spin I there are $(2I+1)$ basis functions for the Hilbert space. These all have a total angular momentum, I , have a z component, m , that goes from $-I$ to $+I$ in steps of 1. We know nothing about these spin states, other than their angular momentum properties. We represent these basis elements as kets with angle brackets $|I, m\rangle$.

Matrix Elements

The spin operators, such as I_x , have the well-known matrix elements amongst the basis functions

$$I_x |I, m\rangle = m |I, m\rangle$$

For more complex interactions, such as the quadrupole coupling, the matrix elements can be calculated by simple extensions of the basic rules.

Commutators

The basic rules are familiar.

$$[I_x, I_x] = 0$$

For more complex interactions, such as the quadrupolar Hamiltonian, the commutators may be more complicated.

$$H_Q = a_Q \left\{ I_x^2 - \frac{1}{3} I^2 + \frac{2}{3} (I_x^2 - I_y^2) \right\}$$

Outline of Theory

In analyzing NMR experiments, we often start by setting up and diagonalizing the Hamiltonian matrix. There is a basis set of angular momentum functions and a set of rules for calculating the matrix elements. The eigenvalues are the energies and the eigenvectors are the wavefunctions of the states. To follow the spin system through time, we define the density matrix, which contains all the transitions and coherences. We then express its time dependence through operator commutators. We then express its time dependence through operator commutators. We then express its time dependence through operator commutators. We then express its time dependence through operator commutators. We then express its time dependence through operator commutators.

The Liouville space method (17-19) we use here is formally very similar. There is a basis set of angular momentum functions derived from the nuclear spin. Instead of the Hamiltonian, we set up and diagonalize the Liouvillian matrix. Again, there is a simple set of rules for calculating the matrix elements. Diagonalizing the Liouvillian gives us the transitions directly - the eigenvalues of the Liouvillian are the resonant frequencies, and the eigenvectors are the coherences. The trace operation becomes the scalar product.

For the particular case of proving the third-order corrections to be zero, the Hamiltonian method requires that we calculate the third-order perturbations (messy!) for each level, and then show they are the same and cancel out. In Liouville space, we work directly with the transition and show the perturbation is zero directly. In particular, a selection rule for the quadrupole interaction (14) is key. The result requires minimal calculation and relies mainly on symmetry.

LIUOVILLIAN METHODS

Basis Set

For a spin I there are $(2I+1)^2$ basis functions for the Liouville space. These have a total angular momentum, I , that runs from 0 to $(2I)$ in steps of 1. Each value of I has a z component, m , that goes from $-I$ to $+I$ in steps of 1. When you sum these numbers up, you get $(2I+1)^2$ basis functions. These basis functions for Liouville space are the same (except for normalization) as the well-known spherical tensor operators. However, we are deliberately suppressing the operator character, since we do not need it. All that we need is the angular momentum properties. We represent these Liouville-space basis elements as kets with round brackets, $|Im\rangle$.

Matrix Elements

The Liouvillian is a superoperator that represents the action of taking the commutator with the Hamiltonian, so all its matrix elements can be calculated by evaluating commutators. However, there are two simplifications. One is that the commutators with spin operators become spin superoperators (20).

$$I_x |Im\rangle = m |Im\rangle$$

Many operators, such as the quadrupole interaction, involve products of spin operators. Things are more complicated for this case, since the commutator of a product is not the product of the commutators.

However, there are explicit formulae for products of spherical tensor operators (21,22). It is easy to extend these rules to derive explicit formulae for commutators - formulae that do not require any details of the operators beyond their angular momentum properties.

PROOF THAT THE THIRD-ORDER TERM IS ZERO

There is a theorem in quantum mechanics (23) 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 (24), the third-order corrections to the transition frequencies are readily calculated.

Let Q be the quadrupole perturbation. The superspin basis operators are eigenfunctions of the Zeeman interaction (14) 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 $|N\rangle$. (25) Let $\nu_k^{(0)}$ be the unperturbed transition and let $\nu_k^{(1)}$ be the small first-order correction to the transition. The unperturbed frequency, $\nu_k^{(0)}$ and its first, second and third-order corrections (23) (the order is given in the superscript) are given by

$$\begin{aligned} \nu_k^{(0)} &= \langle \nu_k^{(0)} | Q | \nu_k^{(0)} \rangle \\ \nu_k^{(1)} &= \langle \nu_k^{(0)} | Q | \nu_k^{(0)} \rangle \\ \nu_k^{(2)} &= \langle \nu_k^{(0)} | Q | \nu_k^{(0)} \rangle - \nu_k^{(0)} \langle \nu_k^{(0)} | \nu_k^{(0)} \rangle \end{aligned}$$

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 $\nu_k^{(1)}$ is given by

$$\nu_k^{(1)} = \sum_N \frac{\langle N | Q | \nu_k^{(0)} \rangle \langle \nu_k^{(0)} | N \rangle}{\nu_k^{(0)} - \nu_N^{(0)}}$$

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 $\nu_k^{(0)}$ has a definite value of its total angular momentum.

In order to calculate the third-order correction, we substitute the expression for the wavefunction into the third-order expression. We are concentrating on the central transition, so the second term in the third-order expression will be dropped.

$$\begin{aligned} \nu_k^{(2)} &= \langle \nu_k^{(0)} | Q | \nu_k^{(1)} \rangle \\ &= \sum_N \sum_M \frac{\langle M | Q | \nu_k^{(0)} \rangle \langle N | Q | \nu_k^{(0)} \rangle \langle M | Q | N \rangle}{\nu_k^{(0)} - \nu_N^{(0)} \nu_M^{(0)} - \nu_k^{(0)} - \nu_N^{(0)}} \end{aligned}$$

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

This means that for the central transition, both terms in the third-order correction will be zero. For the satellites, the first term in equation 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.

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