General solution to axially symmetric quadrupole interaction in nuclear magnetic resonance of solids

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Received November 24, 1986

This paper is dedicated to Professor John T. Edward

B. C. Sanctuary and G. Campolieti. Can. J. Chem. 65, 1746 (1987).

Spins with magnitude I greater than $\frac{1}{2}$ have nuclear electric quadrupole interactions that perturb the Zeeman splitting. To calculate the spin dynamics of multipulse sequences, it is necessary to know how the system evolves between pulses under the quadrupole. Prior work gave specific solution for $\frac{1}{2} < I \le \frac{9}{2}$ in tabulated form. In this paper, a single expression is obtained, which is valid for all I.

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Les spins dont l'amplitude I est plus grande que $\frac{1}{2}$ possèdent des interactions quadrupolaires électriques nucléaires qui perturbent le couplage Zeeman. Dans le but de calculer la dynamique des spins dans des séquences multispins, il est nécessaire de connaître comment le système évolue entre les pulsations, sous l'effet du quadrupole. Un travail antérieur a fourni une solution spécifique, sous la forme de tableau, du cas où $\frac{1}{2} < I \le \frac{9}{2}$. Dans le présent travail, on a obtenu une expression unique qui est valide pour toutes les valeurs de I.

[Traduit par la revue]

I. Introduction

Spin dynamic calculations of multipulse sequences require knowledge of the evolution of the spin system under the interaction Hamiltonian. For solids containing spin $I > \frac{1}{2}$, the nuclear quadrupole interaction often dominates (1). Typically, a principle axis frame is chosen so that two parameters e^2qQ *and* η are required. Solution of this problem in the presence of a magnetic field is difficult as a consequence of the two different symmetries of the Zeeman and quadrupole Hamiltonians. When the asymmetry term η is zero and the principal axis lies along the magnetic field direction, an exact solution is possible. In a previous paper (2) the solutions were given for specific I values from $I = 1$ to $\frac{9}{2}$. Hence the evolution of the full density matrix was obtained from arbitrary initial conditions.

The difficulty with the solutions of ref. 2, although exact, is that they are specific for each I magnitude. No general transformation was found that solved the complete problem for any I. In contrast, knowledge of the transformation that diagonalizes the quadrupole Hamiltonian would allow the symmetry properties to be studied and these, in turn, would aid in finding perturbation solutions when $\eta \neq 0$, that is, when the field and principal axis do not coincide.

In this paper we report the general solution, using the multipole formulations, to the axially symmetric quadrupole problem in which the principal axis and magnetic field direction coincide. The solutions are valid for all I magnitudes. Table 1 of ref. 2 is obviated and a simple expression for all the transformations is given. The results of Table 3 of ref. 2 reduce to one simple equation.

II. Background

The Hamiltonian in question is given by

$$[1] \quad H_Q = -\gamma\hbar I_Z H_Z + \hbar Q_I\{3I_Z^{\,2} - I(I+1)\}$$

where

$$[2] \quad Q_I = \bar{Q}/[2I(2I-1)]$$

The object is to calculate the full spin density matrix, $\sigma_I(t)$, which evolves according to

$$[3] \quad i\hbar \frac{\partial \sigma_I(t)}{\partial t} = [H_Q, \sigma_I]$$

To proceed, the spin density operator is expanded in terms of spherical tensor operators (3, 4),

$$[4] \quad \sigma_I = \frac{1}{2I+1}\left[E_I + \sum_{k=1}^{2I}\sum_{q=-k}^{k} \phi_q^k(t)\mathcal{Y}^{kq}(I)\right]$$

The problem is then to obtain the coefficients $\phi_q^{\,k}(t)$. These are loosely referred to as polarizations with multipole magnitude k and multiquantum coherence q. More exactly, the k even quantities are alignments while the k odd are polarizations. Moreover, $q = 0$ are not coherences but incoherent superpositions of populations for the single spin case. The $q \neq 0$ terms are correctly coherences. These distinctions are not made in this work and all $\phi_q^{\,k}(t)$ are considered polarizations with coherence q.

In the rotating frame, defined by

$$[5] \quad \hat{\phi}_q^{\,k}(t) = \exp(-iq\omega_0 t)\phi_q^{\,k}(t)$$

where $\omega_0 = \gamma H_Z$, the Hamiltonian [1] gives

$$[6] \quad \frac{\partial \hat{\phi}_q^k}{\partial t} = \frac{3}{2}q\bar{Q}\left[\frac{(2I+k+2)(2I-k)[(k+1)^2-q^2]}{I^2(2I-1)^2(2k+1)(2k+3)}\right]^{1/2}\hat{\phi}_q^{k+1} - \frac{3}{2}q\bar{Q}\left[\frac{(2I+k+1)(2I-k+1)[k^2-q^2]}{I^2(2I-1)^2(2k-1)(2k+1)}\right]^{1/2}\hat{\phi}_q^{k-1}$$

It is these sets of coupled equations which have been solved from initial conditions $\phi_q^{\,k}(0)$ for special cases of I and q and which are reported in ref. 2, Tables 1 and 3. As I increases, the dimensionality of the resulting matrices increases. The unitary transformations required to diagonalize these become increasingly difficult to obtain. From Tables 1 and 3 of ref. 2 some inherent symmetries appear to be present, but these are not obvious.

III. Alternate solutions

From eq. [3], the solution to $\sigma(t)$ is

$$[7] \quad \sigma(t) = \exp\left(\frac{-i}{\hbar} H_Q t\right) \sigma(0) \exp\left(\frac{i}{\hbar} H_Q t\right)$$

where

$$\sigma(0) = |\psi(0)\rangle\langle\psi(0)|$$

Using eq. [3] and the orthogonality of the spherical tensor operators

$$[8] \quad \mathrm{Tr}\,\{\mathcal{Y}^{k'q'\dagger}\mathcal{Y}^{kq}\} = (2I+1)\delta_{kk'}\delta_{qq'}$$

where † is the operator adjoint, the density operator becomes

$$[9] \quad \phi_q^k(t) = \frac{1}{2I+1} \sum_{k'q'} \langle\!\langle \mathcal{Y}^{kq} |\, e^{-iH_Q t/\hbar} \mathcal{Y}^{k'q'} e^{iH_Q t/\hbar} \rangle\!\rangle \phi_{q'}^{k'}(0)$$

The inner product is defined

$$[10] \quad \langle\!\langle A|B \rangle\!\rangle = \mathrm{Tr}\,\{A^\dagger B\}$$

The Wigner–Eckart theorem (5, 6) gives

$$[11] \quad \langle IM|\mathcal{Y}^{kq}|I'M'\rangle = \delta_{II'}(-1)^{I-M}\begin{pmatrix} I & k & I \\ -M & q & M' \end{pmatrix} \times \langle I\|\mathcal{Y}^k\|I\rangle$$

where the reduced matrix element is

$$[12] \quad \langle I\|\mathcal{Y}^k\|I\rangle = i^k \cdot \sqrt{(2I+1)(2k+1)}$$

Using this, eq. [9] becomes

$$[13] \quad \hat{\phi}_q^k(t) = \sum_{k'=0}^{2I} \sum_{M=-I}^{I} (i)^{k'-k}\sqrt{(2k+1)(2k'+1)} \times \begin{pmatrix} I & I & k \\ M & -M-q & q \end{pmatrix}\begin{pmatrix} I & I & k' \\ M & -q-M & q \end{pmatrix} \times e^{i3\omega'_Q q(q+2M)t}\phi_q^{k'}(0)$$

with

$$\omega^I{}_Q = -Q_I$$

which is the exact solution for the time evolution of the full density matrix under Hamiltonian [1] from arbitrary initial conditions $\phi^k{}_q(0)$.

IV. Discussion

The multipole operators (7) $\mathcal{Y}^{kq}(I) \equiv |kq\rangle\!\rangle$ are useful for describing pulsed nmr primarily because they are rotated under the Zeeman interaction. In contrast, the quadrupole Hamiltonian is diagonal in the $|IM\rangle\langle IM'|$ basis. The relation between the $|kq\rangle\!\rangle$ and $|IM\rangle\langle IM'|$ basis is

$$[14] \quad |kq\rangle\!\rangle = i^k[(2I+1)(2k+1)]^{1/2}\sum_M (-1)^{I-M} \times \begin{pmatrix} I & k & I \\ -M & q & M-q \end{pmatrix}|IM\rangle\langle IM-q| \equiv (2I+1)^{1/2}\sum_M \mathcal{T}_q^{kM}(I)|IM\rangle\langle IM-q|$$

It then follows that the solution [13] can be written as

$$[15] \quad \hat{\phi}^k{}_q = \sum_{k'}\sum_{M=-I}^{I} (\mathcal{T}(I)^{-1})_q^{q+M,k} \times \exp\,[i3\omega^I{}_Q q(q+2M)t]\mathcal{T}^{k'}{}_q^{q+M}(I)\phi_q^{k'}(0)$$

where

$$[16] \quad (\mathcal{T}(I)^{-1})_q^{Mk} \equiv \mathcal{T}_q^{kM}(I)^*$$

which is to be compared to [23] of ref. 2. Equation [15] generates all the results of Table 3 of ref. 2 while the expression for $\mathcal{T}_q^{kM}(I)$, eq. [14], generates Table 1 of ref. 2.

The symmetries of $\mathcal{T}$ are simply those of 3–j coefficients. Using these and the explicit expressions in eq. [9] will be useful in obtaining perturbative solutions to problems where the principal axis differs from the symmetry axis or when $\eta \neq 0$.

Acknowledgements

This work is supported by a Canadian Government grant (NSERC) and a Quebec Government grant (FCAC).

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