# MULTITRANSITION NUCLEAR RELAXATION IN PRESENCE OF STATIC QUADRUPOLAR INTERACTIONS

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## 1. Introduction

We have used the formalism of fictituous spin 1/2 to describe the nuclear relaxation of spins I>1/2 in solids (1). We found a generalized macroscopic kinetic differential equation for any observable, expanded in a complete basis set of independent fictituous spin 1/2 operators, and whose time evolution is expressed in terms of a matrix of relaxation. The interest of such method was to allow a possible treatment of the relaxation whether for a single or multiple relaxation processes. Several examples were treated for dipolar and quadrupolar relaxations, including the case of a residual time averaged quadrupolar interaction (1).

However there exists some arguments against the choice of a basis of fictituous spin-1/2 operators. Several authors have proposed a description of the spin dynamics in term of an irreducible tensors basis (2, 3). Some have even claimed that the fictituous spin basis cannot reach the physical meaning of a studied phenomenon (3). We show on a particular case that one can obtain, without any calculation, a matrix of relaxation previously calculated (1) by using an energy level diagram which is a pictorial description of the fictituous spin operators.

It was also point out recently that the *fictitious* spin-1/2 basis presents some redundance (4). An alternative way of describing a spin 3/2 was proposed in term of a direct product of two Pauli matrices (Dirac basis (5)). We show that the fictituous spin-1/2 allows to build a basis without such redundance and the correspondance between the Dirac and fictituous spin-1/2 bases is given. We discuss finally some physical reasons to prefer either irreducible tensor or fictituous spins descriptions.

## 2. Relaxation in the case of multilevel systems

In Fig. 1 we have displayed three levels i, j, k of a multilevel system.

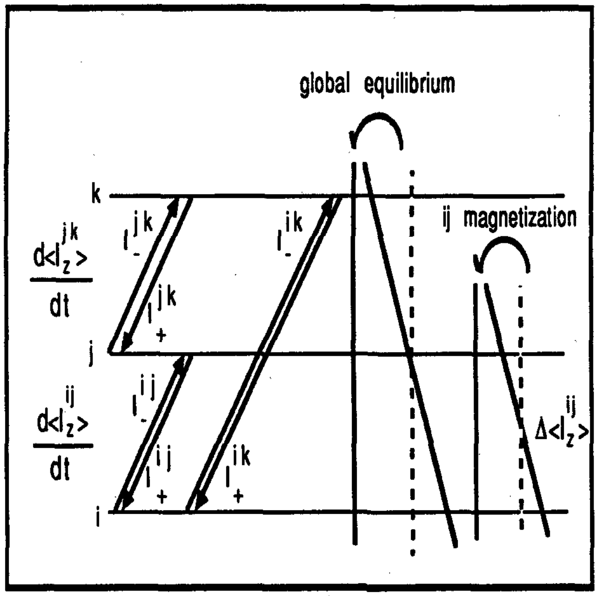


Fig. 1 Schematic description of the longitudinal relaxation of a three-level system, the different transitions are indicated as bold inclined lines, the deviations to global or partial equilibrium are also indicated.

The average of fictitious spin-1/2 operator $\langle I_z^{ij}\rangle$ describes the ij polarisation and the operators $I_+^{ij}$ and $I_-^{ij}$ describe the transitions j=>i and i=>j, respectively. The dynamical variation of the polarisations are expressed by the following kinetic equations

$$\frac{d}{dt}\begin{pmatrix}\langle I_z^{ij}\rangle \\ \langle I_z^{jk}\rangle\end{pmatrix} = -\begin{pmatrix}\frac{1}{T_1^{ij,ij}} & \frac{1}{T_1^{ij,jk}} \\ \frac{1}{T_1^{jk,ij}} & \frac{1}{T_1^{jk,jk}}\end{pmatrix}\begin{pmatrix}\Delta\langle I_z^{ij}\rangle \\ \Delta\langle I_z^{jk}\rangle\end{pmatrix} \quad (1)$$

where the symbol Δ represents the deviation to equilibrium. Each $1/T_1^{ij,jk}$ rate, whose a general expression is given in ref(1), is a linear combination of spectral densities $J(\omega_{ij})$, $\omega_{ij}$ being the transition frequency. In Fig. (1) the inclined bold lines represent the equilibrium distributions of the global or partial ij polarizations. The dashed vertical lines represent the initial distributions in case of saturation experiment. From Eq. (1), $\Delta\langle I_z^{ij}\rangle$ drives the dynamical variations of $\langle I_z^{ij}\rangle$ and $\langle I_z^{jk}\rangle$ through the relaxation rates $1/T_1^{ij,ij}$ and $1/T_1^{jk,ij}$, respectively. A transition has a positive contribution on such relaxation rates if it creates a variation of polarization which favors the return to equilibrium. For instance, the return to equilibrium $\Delta\langle I_z^{ij}\rangle$ let decrease the population of level j. Owing to the transition j => k, it thus results a negative evolution to equilibrium for the polarization $\langle I_z^{jk}\rangle$. In consequence the spectral density $J(\omega_{jk})$ will contribute negatively to $1/T_1^{jk,ij}$. Since the population j of $\langle I_z^{ij}\rangle$ is only involved here, this contribution occurs just once. Similarly the return to equilibrium $\Delta\langle I_z^{ij}\rangle$ increases the population i and the population k decreases due to the transition k=>i. This drives effectively the polarization $\langle I_z^{jk}\rangle$ to equilibrium and yields a positive contribution of $J(\omega_{ik})$ to $1/T_1^{jk,ij}$. Let consider now the $1/T_1^{ij,ij}$ rate. The transition i<=>j let decrease the population j and increases the population i during the return to equilibrium $\Delta\langle I_z^{ij}\rangle$. In consequence the spectral density $J(\omega_{ij})$ contributes positively twice to $1/T_1^{ij,ij}$. This gives finally :

$$\frac{1}{T_1^{jk,ij}} = -\alpha_{ij}J(\omega_{ij}) - \alpha_{jk}J(\omega_{jk}) + \alpha_{ik}J(\omega_{ik}),$$
$$\frac{1}{T_1^{ij,ij}} = +2\,\alpha_{ij}J(\omega_{ij}) + \alpha_{jk}J(\omega_{jk}) + \alpha_{ik}J(\omega_{ik}), \qquad (2)$$

where the $\alpha_{ij}$ are some real positive coefficients immediately calculable in the interacting frame, using Eqs. (10 and 12) of Ref (1). For example in a quadrupolar relaxation process all the $\alpha_{ij}$ are equal.

## 3. Application to quadrupolar relaxation including a residual time averaged interaction

We have presented a comprehensive study of the relaxation of nuclear spins I>1/2 in a previous paper (1) Here we apply the method described above to the quadrupolar relaxation of a nuclear spin I=3/2 in presence of a static or residual time averaged quadrupolar interaction $H_Q$.

The corresponding multilevel system is displayed on Fig. 2.

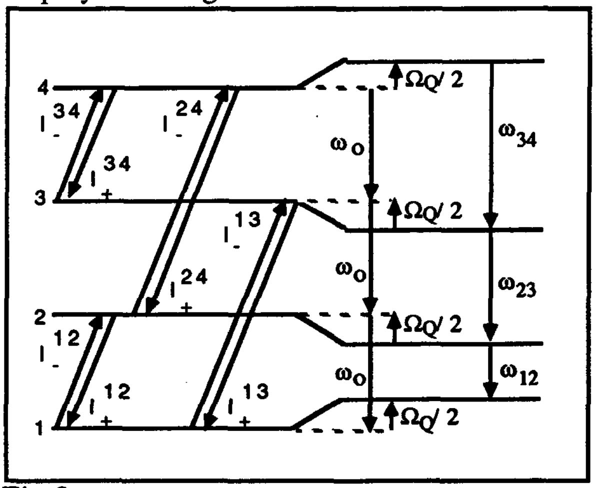


Fig.2 Schematic description of the longitudinal relaxation of a nuclear spin I=3/2 experiencing a high magnetic field and a residual quadrupolar interaction $\Omega_Q$

The dynamical variation of the polarisations are expressed by the following equations :

$$\frac{d}{dt}\begin{pmatrix}\langle I_z^{14}\rangle\\ \langle I_z^{23}\rangle\\ \langle I_z^{12\text{-}34}\rangle\end{pmatrix} = -\begin{pmatrix}\frac{1}{T_1^{14,14}} & \frac{1}{T_1^{14,23}} & \frac{1}{T_1^{14,12\text{-}34}}\\ \frac{1}{T_1^{23,14}} & \frac{1}{T_1^{23,23}} & \frac{1}{T_1^{23,12\text{-}34}}\\ \frac{1}{T_1^{12\text{-}34,14}} & \frac{1}{T_1^{12\text{-}34,23}} & \frac{1}{T_1^{12\text{-}34,12\text{-}34}}\end{pmatrix}\begin{pmatrix}\Delta\langle I_z^{14}\rangle\\ \Delta\langle I_z^{23}\rangle\\ \Delta\langle I_z^{12\text{-}34}\rangle\end{pmatrix} \qquad (3)$$

where the different relaxation rates are given in Table 1. All the coefficients of this Table can be found by a straightforward application of the diagrammatic method exposed in section 2.

It is worthwhile to make a comparison with the usual case of $\Omega_Q = 0$. Substituting $\Omega_Q = 0$ in Table 1 merges the columns (a - b) and (c - d). The longitudinal rates, noted in bold in Eq. (3), vanish. The resulting relaxation matrix is divided in two block matrices of dimension 2x2 and 1x1, respectively. One can show that the former describes the dynamics of the Zeeman order and the latter deals with the quadrupolar order.

As already explained in ref. (1), the "bold" longitudinal coupling rates arise from two factors : (i) the presence of a residual time-averaged interaction (here $\Omega_Q \neq 0$); (ii) a drastic frequency dependence for the spectral density. These two factors are often induced by an anisotropic motion (low dimensionality, restricted motion, ...). The immediate consequence of a motion of low symmetry is indeed to break the symmetry of the relaxation

$$\frac{1}{T_{1Q}^{cd,ef}} = \frac{3}{2} C_Q^2 * \left[ a J_1(\omega_O - \Omega_Q) + b J_1(\omega_O + \Omega_Q) + c J_2(2\omega_O - \Omega_Q) + d J_2(2\omega_O + \Omega_Q) \right]$$

| cd,ef | a | b | c | d |
|---|---|---|---|---|
| 14,14 | 1 | 1 | 1 | 1 |
| 14,23 | -1 | -1 | 1 | 1 |
| 14,12-34 | -1 | 1 | -1 | 1 |
| 23,14=14,23 | | | | |
| 23,23=14,14 | | | | |
| 23,12-34 | 1 | -1 | -1 | 1 |
| 12-34,14 | -2 | 2 | -2 | 2 |
| 12-34,23 | 2 | -2 | -2 | 2 |
| 12-34,12-34 | 2 | 2 | 2 | 2 |

Table 1. Elements of the spin-lattice relaxation rates for the quadrupolar fluctuations in presence of a residual time-averaged quadrupolar splitting $\Omega_Q$.

process itself. For instance in the case treated here, such a motion mixes together the dynamics of the Zeeman and the quadrupolar orders. So the eigendirections of the relaxation process in case of anisotropic motion are a mixture of the Zeeman and quadrupolar eigendirections for isotropic motions.(Eq. (27) of ref. (1).

## 4. Choice of the spin operators basis

We show here that the fictitious spin-1/2 basis does not present any redundance and can be simply related to the other possible bases. This is detailed in Table 2 where we have given the 16 spin operators necessary to describe properly a spin 3/2 successively in the Dirac, fictitious spin 1/2 and irreducible tensors bases.

The presence of a redundance in the fictitious spin 1/2 basis vanishes when choosing the spin operators $A_p$ as follows :

$$A_p \equiv \left\{ I_\alpha^{1j} \pm I_\alpha^{kl} \right\},\ \alpha \in \{x, y, z\},$$
$$j \neq k \neq l \in \{2, 3, 4\},\ p \in \{1, \ldots, 15\} \text{ for } I = \frac{3}{2}$$
$$\text{with } \mathrm{Tr}\{A_p A_q\} = \delta_{pq} \qquad (4)$$

The basis $\{A_p\}$ is completed by addition of the unity operator.

| | | | |
|---|---|---|---|
| $\sigma_1 \otimes \sigma_1$<br>$1$<br>$T_0^0$ | $\sigma_1 \otimes \sigma_x \equiv x_2$<br>$2(I_x^{12}+I_x^{34})$<br>$\frac{-2\sqrt{3}}{5}T_1^1(a)+\frac{-4}{3\sqrt{5}}T_1^3(a)$ | $\sigma_1 \otimes \sigma_y \equiv y_2$<br>$2(I_y^{12}+I_y^{34})$<br>$\frac{2i\sqrt{3}}{5}T_1^1(s)+\frac{4i}{3\sqrt{5}}T_1^3(s)$ | $\sigma_1 \otimes \sigma_z \equiv z_2$<br>$2(I_z^{12}+I_z^{34})$<br>$\frac{2}{5}T_0^1+\frac{8}{3\sqrt{10}}T_0^3$ |
| $\sigma_x \otimes \sigma_1 \equiv x_1$<br>$2(I_x^{13}+I_x^{24})$<br>$\frac{2}{\sqrt{6}}T_2^2(s)$ | $\sigma_x \otimes \sigma_x \equiv x_1x_2$<br>$2(I_x^{14}+I_x^{23})$<br>$\frac{-2}{3}T_3^3(a)+\frac{-2}{5}T_1^1(a)$<br>$+\frac{2}{\sqrt{15}}T_1^3(a)$ | $\sigma_x \otimes \sigma_y \equiv x_1y_2$<br>$2(I_y^{14}-I_y^{23})$<br>$\frac{2i}{3}T_3^3(s)+\frac{-2i}{5}T_1^1(s)$<br>$+\frac{2i}{\sqrt{15}}T_1^3(s)$ | $\sigma_x \otimes \sigma_z \equiv x_1z_2$<br>$2(I_x^{13}-I_x^{24})$<br>$\frac{4}{3\sqrt{2}}T_2^3(s)$ |
| $\sigma_y \otimes \sigma_1 \equiv y_1$<br>$2(I_y^{13}+I_y^{24})$<br>$\frac{-2i}{\sqrt{6}}T_2^2(a)$ | $\sigma_y \otimes \sigma_x \equiv y_1x_2$<br>$2(I_y^{14}+I_y^{23})$<br>$\frac{2i}{3}T_3^3(s)+\frac{2i}{5}T_1^1(s)$<br>$\frac{-2i}{\sqrt{15}}T_1^3(s)$ | $\sigma_y \otimes \sigma_y \equiv y_1y_2$<br>$-2(I_x^{14}-I_x^{23})$<br>$\frac{2}{3}T_2^2(a)+\frac{-2}{5}T_1^1(a)$<br>$+\frac{2}{\sqrt{15}}T_1^3(a)$ | $\sigma_y \otimes \sigma_z \equiv y_1z_2$<br>$2(I_y^{13}-I_y^{24})$<br>$\frac{-4i}{3\sqrt{2}}T_2^3(a)$ |
| $\sigma_z \otimes \sigma_1 \equiv z_1$<br>$2(I_z^{14}+I_z^{23})$<br>$\frac{4}{5}T_0^1-\frac{4}{3\sqrt{10}}T_0^3$ | $\sigma_z \otimes \sigma_x \equiv z_1x_2$<br>$2(I_x^{12}-I_x^{34})$<br>$\frac{-2}{\sqrt{6}}T_1^2(a)$ | $\sigma_z \otimes \sigma_y \equiv z_1y_2$<br>$2(I_y^{12}-I_y^{34})$<br>$\frac{2i}{\sqrt{6}}T_1^2(s)$ | $\sigma_z \otimes \sigma_z \equiv z_1z_2$<br>$2(I_z^{12}-I_z^{34})$<br>$\frac{2}{\sqrt{6}}T_0^2$ |

Table 2 Correspondence between three bases describing a spin 3/2. The notations x, y, z corresponds to those of ref. (4). The definitions and properties of fictituous spin-1/2 can be found in ref. (6). The definitions of irreducible tensors T(a) and T(s) are given in ref. (3).

From Table 2, one notes that there is mainly two kinds of bases. The first kind is composed either of Dirac (product of cartesian spin operators) or fictituous spin-1/2 $\{A_p\}$ bases. The second kind involves the different possibilities to build an irreducible tensor basis (2, 3, 7).

The properties of the $\{A_p\}$ and product of cartesian spin operators bases are so close that in the description of a spin 3/2 with the $\{A_p\}$ basis we can used the same simple picture that the one previously proposed for the product of cartesian spin operators (8). This is precisely what we have displayed in Table 3. For exemple the term $z_1x_2$ describes a x coherence of a spin "2" in antiphase with respect to spin "1". The corresponding $A_p$ term describes the antiphase behavior of the one quantum coherence of the quadrupolar satellites 12 and 34.

Finally we discuss some physical reasons to prefer either irreducible or fictitious spins descriptions. It is difficult to define precisely the domain of application of one description or the other. However, it is often more adapted to use the irreducible tensor description when the evolution operator itself can be seen as a simple rotation.

| | in-phase one quantum x coherence quadrupolar satellite | in-phase one quantum y coherence quadrupolar satellite | polarization involving the Zeeman order |
|---|---|---|---|
| in-phase two quanta x coherence, two quanta quadrupolar satellite | "two-spin" coherence 3q. and central line of 1q. coherences | "two-spin" coherence 3q. and central line of 1q. coherences | antiphase two quanta x coherence, two quanta quadrupolar satellite |
| in-phase two quanta y coherence, two quanta quadrupolar satellite | "two-spin" coherence 3q. and central line of 1q. coherences | "two-spin" coherence 3q. and central line of 1q. coherences | antiphase two quanta y coherence, two quanta quadrupolar satellite |
| polarization involving the Zeeman order | antiphase one quantum x coherence quadrupolar satellite | antiphase one quantum y coherence quadrupolar satellite | longitudinal "two-spin" quadrupolar order |

Table 3 Correspondence between the properties of the $\{A_p\}$ and product of cartesian spin operators bases. The place of each term is the same as in Table 2.

Effectively all the spin components are transformed in such a way that the global object "density matrix of spin 3/2" will not be distorded. For instance an experiment with "hard pulses" can be analyzed in term of rotations. On the other hand, when the evolution operator cannot be reduced to a simple rotation the global "density matrix of spin 3/2" is distorded. For exemple this occurs in experiments with selective pulses. Also the quadrupolar relaxation process in presence of static interactions treated above is another typical exemple. Effectively the mixing of the Zeeman and quadrupolar orders exhibits the break of the rotation symmetry. In this latter case the irreducible tensors would imply a linear combination of spherical tensors of different ranks. At least the fictituous spin-1/2 operators allows to follow directly the dynamics of the different level populations. This is always true because the picture coming from the $\{A_p\}$basis is the more adapted to describe the populations and the transitions of a multilevel system.

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