

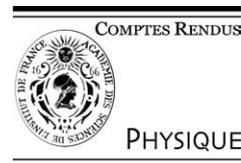


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Highly polarized nuclear spin systems and dipolar interactions in NMR/Systèmes de spins nucléaires fortement polarisés et interactions dipolaires en RMN

Saturation in the quasiadiabatical limit: a time-dependent projection operator formalism approach

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Abstract

This paper presents a new theoretical approach for the description of quasiadiabatic evolution of thermodynamic observables. The new method extends the projection operator technique by considering time-dependent projectors. A master equation is derived in the limit of a slow or adiabatic evolution and is applied to calculate the rate of saturation of dipolar order in a slowly rotating sample. *To cite this article: T. Charpentier et al., C. R. Physique 5 (2004).*

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Résumé

Saturation dans la limite quasiadiabatique : une approche par un formalisme de projecteurs dépendant du temps.

Nous présentons une nouvelle approche théorique pour décrire l'évolution quasiadiabatique de grandeurs thermodynamiques. Cette nouvelle méthode est basée sur la technique des opérateurs de projection mais en considérant des opérateurs dépendant du temps. Une équation pilote est établie dans la limite adiabatique. Nous appliquons notre formalisme pour calculer le taux de saturation de l'ordre dipolaire en présence de rotation lente de l'échantillon. *Pour citer cet article : T. Charpentier et al., C. R. Physique 5 (2004).*

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Mots-clés : Évolution quasiadiabatique ; Grandeurs thermodynamiques ; Technique des opérateurs de projection ; Opérateurs dépendant du temps

1. Introduction

The thermodynamical spin temperature concept is the framework of a general theory of nuclear magnetism in solids which has been extensively studied in the past [1,2]. Numerous theoretical and experimental studies of the evolution of dipolar order under the influence of various external or internal interactions have been carried out. Of particular interest in connection with the present work are studies of the influence of a slow rotation of the sample on the dipolar order [3–5] in high magnetic field. It was first experimentally observed in [3] that the dipolar order lifetime is shortened by sample rotation according to a phenomenological expression of the form $1/T_{1D} = a + bv_{\text{rot}}^2$. From a mathematical point of view, as the samples rotates, the

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dipolar Hamiltonian no longer commutes with itself at different times. Physically, this leads to the saturation of dipolar order because spins are incapable of following the motion and undergo specific (two-particle) lagging out of phase. In [4], the same phenomenon was analyzed experimentally but during spin-locking.

Theoretically, to deal with the problem of a slowly (adiabatically) varying Hamiltonian, a formalism has been described in [5] and the square dependence of the saturation upon the rotation speed was established. Here, we propose a new formal and general theory based on an extension of the Nakajima–Zwanzig projection technique [6,7].

2. The time-dependent projection techniques

The general purpose of the projection operator technique [2] is to decouple a set of configurations of the spin system described by a set of observables of interest, here denoted A_i . The other degrees of freedom are treated as a bath of configurations to which the coupling induces a saturation if coherent motion is considered or a relaxation in the case of incoherent motion. Of great importance is the choice of the A_i operators from which depends the accuracy and the physical relevance of the derived equations. The spin temperature theory [1] is of greatest help in making the correct (relevant) choice of the A_i operators which define a projection super-operator $\hat{\pi}$ as

$$\hat{\pi}(t) = \sum_i \frac{|A_i(t)\rangle\langle A_i(t)|}{\langle A_i(t)|A_i(t)\rangle}, \quad \langle A_i|A_j\rangle = \langle A_i^+ A_j\rangle = \text{Tr}\{A_i^+ A_j\}/\text{Tr}\{1\} \propto \delta_{ij}. \tag{1}$$

The projection super-operator $\hat{\pi}(t) = 1 - \hat{\pi}(t)$ is also introduced. For the sake of simplicity and without loss of generality, we will assume that the A_i are independent observables, i.e., they commute $[A_i(t), A_j(t)] = 0$ at any time, and the Hamiltonian of system can be expanded as $H(t) = \sum_i \alpha_i A_i(t)$. These assumptions hold for most of cases encountered in solid-state NMR experiments.

Let $|\rho(t)\rangle$ be the spin density operator of the system under consideration. It obeys the Liouville–Von Neumann equation

$$\frac{d}{dt}|\rho(t)\rangle = -i|[H(t), \rho(t)] = -i\hat{\mathcal{L}}(t)|\rho(t)\rangle, \tag{2}$$

where $\hat{\mathcal{L}}$ is the time-dependent Liouville super-operator. Similarly to the time-independent case, one can check that

$$\hat{\pi}(t)\hat{\mathcal{L}}(t) = \hat{\mathcal{L}}(t)\hat{\pi}(t) = 0, \quad \text{and} \quad \hat{\pi}(t)\hat{\mathcal{L}}(t) = \hat{\mathcal{L}}(t)\hat{\pi}(t) = \hat{\mathcal{L}}(t). \tag{3}$$

Multiplying Eq. (2) on the left by $\hat{\pi}(t)$ and $\hat{\pi}(t)$, and applying Eqs. (3) leads to

$$\hat{\pi}(t)\frac{d}{dt}|\rho(t)\rangle = -i\hat{\pi}(t)\hat{\mathcal{L}}(t)|\rho(t)\rangle = 0, \tag{4}$$

$$\hat{\pi}(t)\frac{d}{dt}|\rho(t)\rangle = -i\hat{\pi}(t)\hat{\mathcal{L}}(t)(\hat{\pi}(t) + \hat{\pi}(t))|\rho(t)\rangle = -i\hat{\mathcal{L}}(t)\hat{\pi}(t)|\rho(t)\rangle. \tag{5}$$

We introduce the super-operators $\dot{\hat{\pi}}(t) = d\hat{\pi}(t)/dt$, and $\dot{\hat{\pi}}(t) = -\dot{\hat{\pi}}(t)$ in order to evaluate the time derivative of the ‘diagonal’ and ‘off-diagonal’ parts of the density operator ($\hat{\pi}|\rho\rangle$ and $\hat{\pi}|\rho\rangle$, respectively) as follows

$$\frac{d}{dt}(\hat{\pi}|\rho\rangle) = \dot{\hat{\pi}}|\rho\rangle + \hat{\pi}\frac{d}{dt}|\rho\rangle = \dot{\hat{\pi}}\hat{\pi}|\rho\rangle + \dot{\hat{\pi}}\hat{\pi}|\rho\rangle, \tag{6}$$

$$\frac{d}{dt}(\hat{\pi}|\rho\rangle) = \dot{\hat{\pi}}|\rho\rangle + \hat{\pi}\frac{d}{dt}|\rho\rangle = \dot{\hat{\pi}}(\hat{\pi} + \hat{\pi})|\rho\rangle - i\hat{\mathcal{L}}\hat{\pi}|\rho\rangle = -\dot{\hat{\pi}}\hat{\pi}|\rho\rangle - i(\hat{\mathcal{L}} - i\dot{\hat{\pi}})\hat{\pi}|\rho\rangle. \tag{7}$$

Eq. (7) can be formally integrated to

$$\hat{\pi}(t)|\rho(t)\rangle = \hat{S}(t, 0)\hat{\pi}(0)|\rho(0)\rangle - \int_0^t \hat{S}(t, \tau)\dot{\hat{\pi}}(\tau)\hat{\pi}(\tau)|\rho(\tau)\rangle d\tau, \tag{8}$$

where

$$\hat{S}(t, \tau) = \hat{T} \exp \left\{ -i \int_{\tau}^t (\hat{\mathcal{L}}(u) - i\dot{\hat{\pi}}(u)) du \right\}. \tag{9}$$

Assuming that, at time $t = 0$, ρ is ‘diagonal’ (i.e., $\hat{\pi}(0)|\rho(0)\rangle = 0$), and inserting Eq. (8) in Eq. (6), we arrive at the master equation

$$\frac{d}{dt}(\hat{\pi}(t)|\rho(t)\rangle) = \dot{\hat{\pi}}(t)\hat{\pi}(t)|\rho(t)\rangle - \dot{\hat{\pi}}(t) \int_0^t \widehat{S}(t, \tau)\dot{\hat{\pi}}(\tau)\hat{\pi}(\tau)|\rho(\tau)\rangle d\tau. \tag{10}$$

The use of the relation $\dot{\hat{\pi}}\hat{\pi} = -\hat{\pi}\dot{\hat{\pi}}$ shows that when multiplying on the left Eq. (10) by $\langle A_i(t)|$, the first term of the right-hand side cancels. Consequently, this term does not play any role in the evolution of the ‘diagonal’ part of the density operator. We shall therefore prefer the following final form of the master equation (making use of $\hat{\pi}\dot{\hat{\pi}}\hat{\pi} = 0$)

$$\hat{\pi}(t) \frac{d}{dt}(\hat{\pi}(t)|\rho(t)\rangle) = -\hat{\pi}(t)\dot{\hat{\pi}}(t) \int_0^t \widehat{S}(t, \tau)\dot{\hat{\pi}}(\tau)\hat{\pi}(\tau)|\rho(\tau)\rangle d\tau. \tag{11}$$

This form is very similar to the time-independent form but with a modified super-propagator and having $\hat{\pi}$ playing the role of the perturbation, as expected.

3. Evolution of the dipolar spin temperature

We apply now our formalism to calculate the rate of saturation of the dipolar order in a slowly rotating sample at spin rate $\omega_{\text{rot}} = 2\pi\nu_{\text{rot}}$. The observable of interest is the secular part of the dipolar Hamiltonian, denoted $H_D(t)$, as the Zeeman order is not affected by this motion ($[I_Z, H_D(t)] = 0$). Consequently, the projection super-operator is

$$\hat{\pi}(t) = \frac{|1\rangle\langle 1|}{\langle 1|1\rangle} + \frac{|H_D(t)\rangle\langle H_D(t)|}{\langle H_D(t)|H_D(t)\rangle}, \tag{12}$$

and, as a result, the ‘diagonal’ part of the density operator

$$\hat{\pi}(t)|\rho(t)\rangle = |1\rangle - \beta_D(t)|H_D(t)\rangle, \tag{13}$$

where $\beta_D(t)$ is the dipolar (inverse) spin temperature. The purpose of the present section is to obtain the master equation of $\beta_D(t)$. Starting from Eq. (11), multiplying the left-hand side term by $\langle H_D(t)|$ gives

$$\langle H_D(t)| \frac{d}{dt}(\beta_D(t)|H_D(t)\rangle) = \dot{\beta}_D(t)\langle H_D(t)^2\rangle + \frac{\beta_D(t)}{2} \frac{d}{dt}\langle H_D(t)^2\rangle. \tag{14}$$

Introducing $|D\rangle = \dot{\hat{\pi}}|H_D\rangle$,

$$|D\rangle = \dot{\hat{\pi}}|H_D\rangle = |\dot{H}_D\rangle - \frac{\langle H_D|\dot{H}_D\rangle}{\langle H_D^2\rangle}|H_D\rangle, \tag{15}$$

we obtain

$$\frac{d}{dt}\beta_D = \frac{\beta_D(t)}{2} \frac{d}{dt}\langle H_D(t)^2\rangle - \int_0^t M(t, \tau)\beta_D(\tau) d\tau, \tag{16}$$

where the memory function $M(t, \tau)$ is defined as

$$M(t, \tau) = \frac{1}{\langle H_D(t)^2\rangle} \langle D(t)|\widehat{S}(t, \tau)|D(\tau)\rangle. \tag{17}$$

It can be easily checked from Eq. (15) that $|D(t)\rangle$ is orthogonal to $|H_D(t)\rangle$ (i.e., $\langle D(t)|H_D(t)\rangle = 0$). Furthermore, one recognizes the first term of the right-hand side of Eq. (16) as being the adiabatic contribution to the evolution of the dipolar spin temperature. It is therefore useful to introduce a new slow varying spin temperature $\widetilde{\beta}_D$ defined as

$$\beta_D(t) = \left\{ \frac{H_D(0)^2}{H_D(t)^2} \right\}^{1/2} \widetilde{\beta}_D(t), \tag{18}$$

which evolves as

$$\frac{d}{dt}\widetilde{\beta}_D = - \int_0^t \widetilde{M}(t, t - \tau)\widetilde{\beta}_D(t - \tau) d\tau, \tag{19}$$

where the memory function, within this *adiabatic frame*, is

$$\tilde{M}(t, t - \tau) = \frac{\langle D(t) | \hat{S}(t, t - \tau) | D(t - \tau) \rangle}{\sqrt{\langle H_D(t)^2 \rangle \langle H_D(t - \tau)^2 \rangle}}. \quad (20)$$

Eqs. (19) and (20) are exact and can be applied to any kind of motion of the sample. Simplifications are introduced in the next section.

4. Formal calculation of the saturation rate

Considering the nature of the spin system under consideration, some approximations can be made which simplify the previous equations into a tractable form. First, we assume that the rotation is sufficiently slow so that the contribution of the term $i\hat{\tau}(u)$ in Eq. (9) can be fully neglected with respect to $\hat{L}(u)$. Secondly, as a function of τ , $\tilde{M}(t, t - \tau)$ decreases in a time which is of the same order of magnitude as T_2 . This time is much shorter than the period of rotation so that we can neglect the variations of $\hat{L}(u)$ in Eq. (9), as well as differences between $H_D(t)$ and $H_D(t - \tau)$, and between $D(t)$ and $D(t - \tau)$. Accordingly, for short time $\tau (\lesssim T_2)$, Eq. (20) can be simplified into

$$\tilde{M}(t, t - \tau) = \frac{1}{\langle H_D(t)^2 \rangle} \langle D(t) | \exp\{-i\hat{L}(t)\tau\} | D(t) \rangle. \quad (21)$$

As we consider time t much longer than T_2 , the upper limit of integration of Eq. (19) can be extended to ∞ giving

$$\frac{d}{dt} \tilde{\beta}_D = -W(t) \tilde{\beta}_D(t), \quad (22)$$

where the saturation rate $W(t)$ is

$$W(t) = \frac{1}{\langle H_D(t)^2 \rangle} \int_0^\infty \langle D(t) | \exp\{-i\hat{L}(t)\tau\} | D(t) \rangle d\tau. \quad (23)$$

At this stage, we introduce the autocorrelation function $f(t, \tau)$

$$f(t, \tau) = \frac{1}{\langle D(t)^2 \rangle} \langle D(t) | \exp\{-i\hat{L}(t)\tau\} | D(t) \rangle. \quad (24)$$

A natural time scale for the dependence of $f(t, \tau)$ on the time τ can be defined by an instantaneous second moment $m(t)$

$$m(t) = \frac{\langle [D(t), H_D(t)] [H_D(t), D(t)] \rangle}{\langle D(t)^2 \rangle}. \quad (25)$$

Using $f(t, \tau)$ (Eq. (24)) and $m(t)$ (Eq. (25)), the saturation rate (Eq. (23)) can be transformed into

$$W(t) = \frac{A(t)}{\sqrt{m(t)}} \frac{\langle D(t)^2 \rangle}{\langle H_D(t)^2 \rangle} \quad (26)$$

where $A(t)$ is a dimensionless quantity

$$A(t) = \int_0^\infty f\left(t, \frac{\tau}{\sqrt{m(t)}}\right) d\tau. \quad (27)$$

One can see clearly the advantages of Eq. (26) in the evaluation of the saturation rate: calculation of $m(t)$, $\langle D(t)^2 \rangle$ and $\langle H_D(t)^2 \rangle$ implies lattice sums over groups of three spins; only the evaluation of $A(t)$, which is dimensionless and of the order of unity, requires some assumptions for modelling $f(t, \tau)$. As an example, using a Gaussian model

$$f(t, \tau) = \exp\left(-\frac{m(t)\tau^2}{2}\right), \quad (28)$$

a time-independent value of $A(t)$ is obtained: $A(t) = \sqrt{\pi/2}$. In order of magnitude $m(t) \sim M_2 = 3\omega_{\text{loc}}^2$ (M_2 is the second moment of the static spectrum and ω_{loc} is the local frequency) and $\langle D(t)^2 \rangle \propto \omega_{\text{rot}}^2 \langle H_D(t)^2 \rangle$, the order of magnitude of the saturation rate is

$$W(t) \propto \frac{\omega_{\text{rot}}^2}{\omega_{\text{loc}}} \quad (29)$$

in agreement with previous approaches [3–5]. Moreover, after some straightforward calculations (see 6), it turns out that our expression of the saturation rate Eq. (26) is identical to Eqs.(31) and (32) of [5]. If both approaches rely on the same approximations (the system can be characterized by a single (dipolar) spin temperature and $\omega_{rot} \cdot T_2 \ll 1$), the formalisms differ completely. The present one is a natural extension of the Nakijima–Zwanzig [6,7] (time-independent) projection operators techniques, widely applied in nonequilibrium statistical mechanics.

5. Application to a powder sample of adamantane

5.1. Experimental results

Experiments have been performed on a Bruker Avance 300 NMR spectrometer using a commercial Bruker MAS 4 mm o.d. probe and a powder sample of adamantane rotating at the magic angle. Jeener–Broekaert sequence [8] has been used for the measurements of the dipolar spin temperature at different spinning speeds. Results of the experiments are shown in Fig. 1. It is seen that each saturation curve can be well fitted using a single exponential decay. As shown in Fig. 1 (bottom), variation of the saturation rate upon the spinning speed is in good agreement with Eq. (29).

5.2. Calculation of the saturation rate

From Eqs. (18) and (22), the evolution of dipolar spin temperature is given by

$$\beta_D(t) = \beta_D(0) \left(\frac{\langle H_D(0)^2 \rangle}{\langle H_D(t)^2 \rangle} \right)^{1/2} \exp \left\{ - \int_0^t W(u) du \right\}. \quad (30)$$

For a powder sample, Eq. (30) must be averaged over all orientations. This averaging is denoted as $\langle \cdot \rangle_{pc}$ in the remainder of the text. Using the Gaussian approximation (Eqs. (27) and (28)), and considering the Jeener–Broekaert sequence [8] for

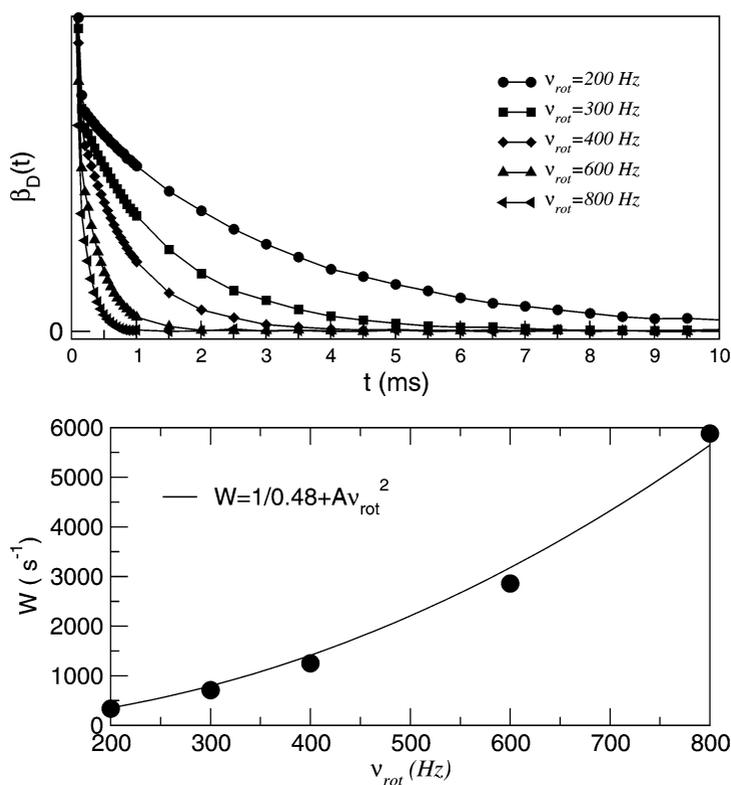


Fig. 1. Top: Variation of the dipolar spin temperature $\beta_D(t)$ in a rotating adamantane powder sample at the magic angle. Solid lines represent the fits of the experimental data using single exponential decays $\exp(-Wt)$. Bottom: variation of the saturation rate W with respect to ν_{rot} . In the non-rotating sample, $T_{1D} = 0.48$ s and $A = 0.00882$ s.

preparing the dipolar order, Eq. (30) has been evaluated numerically for adamantane sample rotating at 200 Hz (calculations will be detailed elsewhere). The resulting curve $\langle \beta_D(t) \rangle_{\text{pc}}$ (data not shown)

$$\langle \beta_D(t) \rangle_{\text{pc}} = \left\langle \beta_D(0) \left(\frac{\langle H_D(0)^2 \rangle}{\langle H_D(t)^2 \rangle} \right)^{1/2} \exp \left\{ - \int_0^t W(\tau) d\tau \right\} \right\rangle_{\text{pc}}, \quad (31)$$

can be fitted very accurately by a single exponential decay with a saturation rate $W_{\text{num}} = 216$ Hz. Thus, we expect that Eq. (31) can be approximated as

$$\langle \beta_D(t) \rangle_{\text{pc}} \approx \left\langle \beta_D(0) \left(\frac{\langle H_D(0)^2 \rangle}{\langle H_D(t)^2 \rangle} \right)^{1/2} \right\rangle_{\text{pc}} \exp \{ - \langle W \rangle_{\text{pc}} t \}. \quad (32)$$

Using this approximation $\langle W \rangle_{\text{pc}}$ is time-independent and a numerical calculation gives $\langle W \rangle_{\text{pc}} = 218$ Hz, very close to W_{num} . Experimental value is $W_{\text{exp}} = 337$ Hz, in satisfactory agreement with our calculations, considering the simple model for the autocorrelation function $f(t, \tau)$ (Eq. (24)). A more sophisticated model will be presented elsewhere.

6. Conclusion

A new theoretical approach has been proposed for the description of quasiadiabatical saturation phenomena. The method is rigorous and general and reproduce the results of Jeener et al. [5] using a quite different mathematical formalism. We hope that the present method can be applied to many other problems.

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Appendix

The aim of this appendix is to show that Eqs. (22)–(24) give the same result as Eqs. 27J and 28J. Here and below the letter ‘J’ in the equation number indicates, that the equation is taken from [5]. The dimensionless observable of interest $\widehat{\mathcal{H}}(t)$, as defined in Eq. 7J, can be connected to $H_D(t)$ through

$$\widehat{\mathcal{H}}(t) = \frac{H_D(t)}{\langle H_D(t)^2 \rangle^{1/2}}, \quad (33)$$

giving

$$\frac{d}{dt} \widehat{\mathcal{H}}(t) = \frac{D(t)}{\langle H_D(t)^2 \rangle^{1/2}}. \quad (34)$$

It is evident from Eqs. 27J and 28J that the function $C(t - t_1)$ is $C(t_0, t - t_1)$, because of its dependence upon t_0 . Within the expected range of applicability of these equations we should choose $t_0 = t$ in $C(t_0, t - t_1)$ and in $\widehat{\mathcal{H}}(t_0)$ on right-hand side of Eq. 27J. Now we see that $C(t, t - t_1)$ coincides with our $f(t, t - t_1)$ (Eq. (24)), and with these corrections Eqs. 27J and 28J coincides with our Eqs. (22)–(24). Of course, the results coincide after introducing of Gaussian approximation (Eq. (28)) and (Eq. 31J) for $f(t, t - t_1) = C(t, t - t_1)$.

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