Appl. Magn. Reson. (2008) 34, 219–226
DOI 10.1007/s00723-008-0114-8
Printed in The Netherlands

Applied Magnetic Resonance

Overview of Spin Temperature, Thermal Mixing and Dynamic Nuclear Polarization

M. Goldman

Commissariat à l'Énergie Atomique de Saclay, Gif-sur-Yvette, France

Received 24 October 2007

Abstract. The aim of this short article is to give a very schematic account of the main concepts associated with the spin temperature theory, in nuclear and in dilute electronic spin systems, and their applications to electron–nuclear thermal mixing as a mechanism of dynamic nuclear polarization. The body of existing theoretical and experimental material on these subjects is much too large to be described in any detail, and a selection can be found in the general references and in references therein.

1 Introduction

The concept of spin temperature, initially for nuclear spin systems, arose under the pressure of experimental facts and gave rise to extensive developments, both theoretical and experimental, meeting with ever increasing success. It was soon found, in succession, that this concept was also valid for electron spin systems at low concentration in insulating solids, that under favourable conditions the electronic spin–spin interactions could be in good thermal contact with the distribution of electronic resonance frequencies as well as with the nuclear Zeeman interactions, and that dynamic nuclear polarization (DNP) could be described in a realistic, sometimes even quantitative manner by the interplay of coupling of this composite thermal reservoir with the electronic Zeeman interaction under off-electronic-resonance microwave irradiation, and spin–lattice relaxation. The rest of this article is a schematic presentation of the main steps of this evolution.

2 The Concept of Spin Temperature [1–3]

When a macroscopic spin system is subjected to the following conditions: it is practically isolated from the external world (the lattice), its interactions are time-independent, energy-conserving transitions can take place between its eigenlevels and are able to rearrange their populations, these populations evolve towards a steady state corresponding to their most probable values. When the only conserved quantities are the number of particles and the energy (the so-called constants of the motion), this corresponds to the Boltzmann distribution of populations:

$$p_i \propto \exp(-E_i / kT), \tag{1}$$

where k is the Boltzmann constant and T is the temperature.

In the usual notations, energies are expressed as frequencies $E = \hbar\omega$, and temperature through the so-called “inverse temperature” $\beta = \hbar/kT$, and Eq. (1) reads:

$$p_i \propto \exp(-\beta\omega_i). \tag{2}$$

More compactly, using the Hamiltonian $\mathcal{H}$ and the spin density matrix σ, we have:

$$\sigma = \exp(-\beta\mathcal{H}) / \mathrm{Tr}\big(\exp(-\beta\mathcal{H})\big). \tag{3}$$

The great advantage of this form is that it can be used even when the Hamiltonian is so complicated as to make it impossible to know its eigenlevels in detail, in particular when the energy spectrum is quasicontinuous.

In the high-temperature limit $\beta\omega \ll 1$, i.e., $E \ll kT$, one uses a first-order expansion of Eq. (3) in inverse temperature:

$$\sigma \simeq 1 - \beta\mathcal{H}.$$

Important remark: a spin system has an upper as well as a lower bound to its energy spectrum. It is then possible to impart to it an energy larger than that corresponding to equal populations for all levels. By convention, the system energy in this last case is set equal to 0. According to Eq. (3), it corresponds to $\beta = 0$. For a system with positive total energy, in the steady state the populations will be higher the higher the level energy and, from the Boltzmann Eq. (2) this system must be assigned a negative value of β, that is, a negative absolute temperature. This causes no problem and it has been extensively justified by experiment. Figure 1 illustrates the population distribution for a system with positive or negative temperature.

2.1 Cases When the Energy Spectrum Is Quasicontinuous

Spin–spin (dipolar) interactions in zero or low field (i.e., such that the Zeeman splitting is not large compared with the spin–spin energy spread). One does not know the eigenlevels, or the type of transitions taking place. It is a case where the energy is the only obvious constant of the motion.

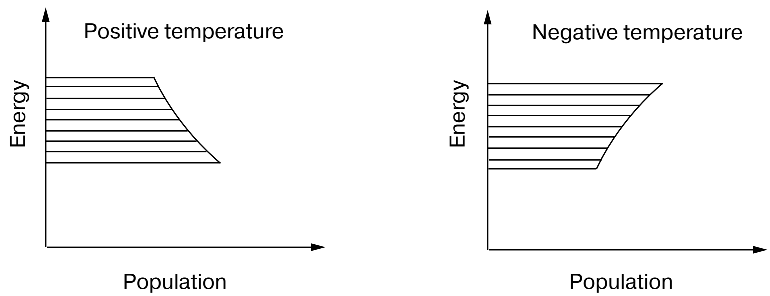

Fig. 1. Boltzmann distribution of populations as a function of energy, for a quasicontinuous system with energy spectrum bounded upwards and downwards, for positive and negative temperatures.

Secular spin–spin interactions in the rotating frame, with zero or small effective field. In this case, one speaks of a spin temperature in the rotating frame. The transitions enabling the redistribution of population among the effective interaction levels are flip-flop transitions of two spins between Zeeman levels.

An obvious condition is that the system contains interacting spins in macroscopic number, comparable with the Avogadro number. This imposes that the sample be solid.

2.2 Case When the Spectrum Is Discrete

It is the case for the Zeeman levels of a homonuclear spin system with spins larger than 1/2. The transitions are, for instance, that of a spin from level m to $m + 1$, and another one from level n to $n - 1$.

2.3 Cases When There Are Several Constants of the Motion

Homonuclear spin system in high field. The Zeeman splitting is so much larger than the quasicontinuous spread of secular spin–spin interactions that it is impossible to have energy-conserving transitions simultaneously changing the Zeeman and the spin–spin energies. The Zeeman and the spin–spin terms are independent energy reservoirs and, in the steady state, the system is characterized by two different temperatures. Figure 2 illustrates that case.

Homonuclear system of spins larger than 1/2 with quadrupole interactions in addition to Zeeman interactions. The spacing between discrete levels being much larger than the spin-spin width, flip-flop transitions rearranging the populations of the discrete levels are impossible, and the system is characterized by as many temperatures as it has independent constants of the motion.

Heteronuclear spin systems. The Zeeman splittings being different, each species is characterized by its own Zeeman temperature. However, the secular spin–spin reservoir is common to all spins.

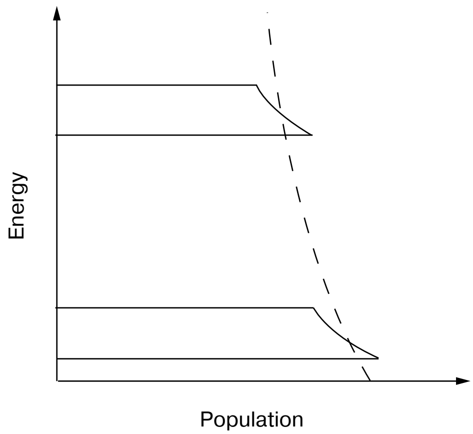

Fig. 2. Energy population distribution for a system with two constants of the motion: Zeeman and secular spin–spin interactions, corresponding to two different temperatures.

2.4 Conditions and Limitations for the Existence of Spin Temperatures

They are largely dictated by considerations of dynamics. Starting from nonequilibrium, the time necessary for the system to reach a steady state is of the order of the inverse of the spin–spin spectral width, that is, of the order of T_2, the transverse decay time of the free induction decay (FID). On the other hand, the spin system is not isolated, but it is coupled to the lattice, and it evolves towards thermal equilibrium with the latter, with time constant equal to the spin–lattice relaxation time, either that of the spin–spin interactions, T_{1D}, or that of the Zeeman or quadrupole interactions, both simply called T_1. Therefore, the steady state with one or several spin temperatures distinct from the lattice temperature is only a quasiequilibrium state which exists on a limited timescale, intermediate between T_2 and T_1. It implies that T_2 be much shorter than T_1, another characteristics of solids.

2.5 Thermal Mixing between Two Thermal Reservoirs

The most common type is the mixing between Zeeman and spin–spin reservoirs, but also sometimes between sets of discrete levels. The mixing can be produced by radio-frequency (rf) irradiation close to the resonance frequency for the case of Zeeman and spin–spin interactions, or by spin–spin interactions for level crossings. It leads to an equalization of their respective temperatures.

In the high-temperature case, the dynamics of the thermal mixing can be quantitatively accounted for by the Provotorov theory [2]. In the case of low temperatures, there exists no fundamental theory for this dynamics.

3 Electronic Spin at Low Concentration in Relation to Nuclear Spins

Convenient basic references are 4 and 5.

It has been shown by experience that electronic spins at low concentration in solids can also reach a steady state characterized by a spin temperature associated with their Zeeman interactions, and under favorable conditions another one associated with their so-called non-Zeeman interactions, consisting of the secular dipole–dipole and hyperfine interactions together with the inhomogeneous interactions associated with distributions or anisotropies of their *g*-factors, provided the latter is not too large.

A particularly favorable case is that when the distance of closest approach of electronic spins is small, of an order comparable to the internuclear distances. In that case it can be shown both experimentally and theoretically that the frequency width over which the spectral diffusion of the non-Zeeman term extends is considerably larger than the EPR line width, and it undergoes a thermal mixing with the nuclear Zeeman reservoirs. This shows up spectacularly when two different nuclear species are present by the following experiment. When after dynamic polarization one of the nuclear species is saturated, both nuclear magnetizations evolve towards a common spin temperature before decaying at their much slower relaxation rate towards thermal equilibrium with the lattice. It is worth insisting on the fact that this thermal mixing requires neither rf nor microwave (mw) excitation.

There are known counterexamples: in compounds where the distance of closest approach between paramagnetic centres is not small, this kind of thermal mixing between electronic non-Zeeman and nuclear Zeeman reservoirs does not exist.

4 Dynamic Nuclear Polarization by Thermal Mixing

The mechanisms put to work are the following. Microwave irradiation close to the electronic resonance frequency produces a change of the non-Zeeman electronic energy: towards lower or higher energy when the irradiation frequency is below or above the electronic Larmor frequency, respectively.

Through thermal mixing the electronic non-Zeeman reservoir is in close thermal contact with the nuclear Zeeman reservoir and their common spin temperature evolves towards a positive or negative value when the irradiation frequency is below or above the electronic Larmor frequency, respectively. The system is then characterized by two temperatures, one for the electronic term and one for the combined electronic non-Zeeman plus nuclear Zeeman terms.

All parts of the system are furthermore coupled to the lattice and experience relaxation. The heat capacity of the nuclear Zeeman term being much larger than that of the electronic non-Zeeman term, because of the high dilution of electronic spins, the relaxation time of the combined electronic non-Zeeman plus

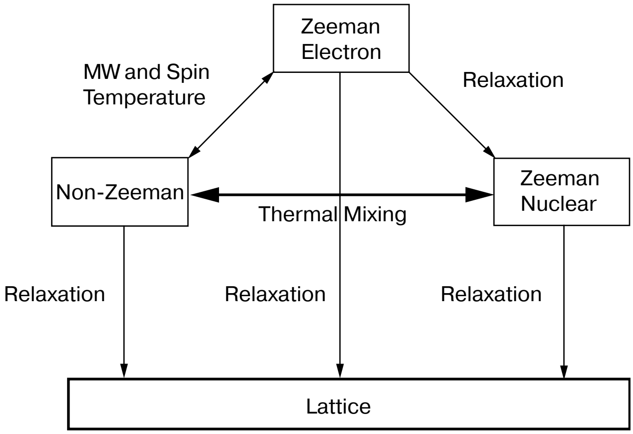

Fig. 3. Block diagram of thermal couplings between four thermal reservoirs: electronic Zeeman, electronic non-Zeeman, nuclear Zeeman and lattice, in the course of DNP under microwave irradiation.

nuclear Zeeman reservoir is much longer than that of the electronic Zeeman reservoir, T_{1e}.

The balance between the different mechanisms determines both the rate and the steady state of the dynamic nuclear polarization.

This is schematically depicted in Fig. 3.

5 Model of Spin Packets

The electronic paramagnetic resonance (EPR) line is quite generally much broader than under the sole effect of the secular dipole–dipole interactions between electronic spins. The model consists in describing it as a sum of contiguous spin packets with different EPR frequencies, each one having well-defined low-energy and high-energy populations. The dipolar-induced flip-flops ensure the continuous existence of a distribution of populations among the various energy levels characterized by two spin temperatures common to all spin packets through the line in the absence of mw irradiation.

One must distinguish two different cases, that when the line broadening is produced by a distribution of g-factors, and that when it arises from the interactions with neighboring nuclear spins, mostly scalar contact interactions.

In the case of inhomogeneous broadening by a distribution of g-factors, each spin packet always keeps its identity. The only possible electronic relaxation transitions are between its low-energy and high-energy levels, therefore its total population remains constant, and its sole evolution is that of its polarization, that is, of the population ratio between its levels.

In the case of a broadening by electronic–nuclear scalar interactions, each packet corresponds to a given set of values of I_z for the surrounding nuclear spins.

The nonsecular part of the interaction between the electronic spins produces a small admixture of the high (resp. low) electronic energy levels of a given spin packet with the low (resp. high) energy levels of different spin packets at adjacent frequencies. As a consequence, electronic relaxation transitions take place not only between the levels of each spin packet but also, with a smaller probability, between levels of adjacent spin packets: the population of each spin packet may vary as well as its polarization.

In all cases, the mw irradiation is assumed to induce transitions on one spin packet only and to be sufficiently strong to saturate it so that its polarization constantly vanishes. Writing that this polarization is zero fixes the ratio of the two spin temperatures, and the state of the system depends on one parameter only. For the rest, the qualitative difference between the two sources of line broadening results in a qualitative difference of the DNP progress in the course of mw irradiation. This difference is limited to the case when the thermal equilibrium electronic polarization is large. Then, one cannot use the linear approximation for the spin temperatures, and the expectation values of the two thermal reservoirs, electronic Zeeman and electronic non-Zeeman plus nuclear Zeeman, depend on both temperatures.

When the line width originates from a g-factor distribution, the polarizations of the various spin packets simply vary along the EPR line in a way which depends on the irradiation frequency as well as on the nuclear polarization and which can be calculated within a given model for the spin packets distribution. For each sign of nuclear polarization there is one well-defined optimum irradiation frequency for optimum DNP efficiency.

When the line is broadened by nuclear scalar interactions, the coupled nuclear spins get polarized as well as the nuclear spins of the bulk. Then, not only the polarizations of the various spin packets depend on the nuclear polarization but also their populations. It can be shown that the packets close to the irradiated one get depopulated to such an extent that the EPR line is displaced: it “slips” away from the irradiation frequency and would bring the polarization to an end unless one “runs” after the line, that is, modifies the irradiation frequency in the course of the DNP, but not so fast as to pass the effective line center, which would make the nuclear polarization to decrease towards a polarization of opposite sign. The rate of change of the irradiation frequency for optimum polarization rate and limit is difficult to predict from theory and it must be determined experimentally for each case.

Despite its approximate character, the spin packet model proves to be in good qualitative agreement with experiment in a number of practical cases, as regards both the progress of the polarization in the course of DNP and its final value. As for the polarization rate, it is very model-dependent and it cannot be predicted with any accuracy.

In a number of cases the final polarization remains miserably low despite all efforts, probably because of a nuclear relaxation leakage originating from sources other than the known paramagnetic centers. One has no control over them as to their characteristics, their concentration or their elimination.

References

1. Abragam, A.: Principles of Nuclear Magnetism, chapt. V and XII. Oxford University Press, Oxford (1961)
2. Goldman, M.: Spin Temperature and Nuclear Magnetic Resonance in Solids. Oxford University Press, Oxford (1970)
3. Goldman, M., in: Maraviglia, B. (ed.) Nuclear Magnetic Double Resonance, Varenna on Lake Como, Villa Monastero, 13–21 October 1992, pp. 1–68. North-Holland, Amsterdam (1993)
4. Abragam, A., Goldman, M.: Rep. Prog. Phys. **41**, 395 (1978)
5. Abragam, A., Goldman, M.: Nuclear Magnetism: Order and Disorder, chapt. 6. Clarendon, Oxford (1982)

Author's address: Maurice Goldman, Commissariat à l'Énergie Atomique de Saclay, 91191 Gif-sur-Yvette, France
E-mail: m.goldman@orange.fr