



# Dynamic nuclear polarization via thermal mixing: Beyond the high temperature approximation



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## ARTICLE INFO

### Article history:

Received 13 December 2016

Revised 26 January 2017

Accepted 29 January 2017

Available online 20 February 2017

### Keywords:

Dynamic nuclear polarization

Hyperpolarization

Thermal mixing

Low spin temperature

## ABSTRACT

Dynamic Nuclear Polarization (DNP) via the mechanism of thermal mixing has proven itself most powerful for the orientation of nuclear spins in polarized targets and hyperpolarization for magnetic resonance imaging (MRI). Unfortunately, theoretical descriptions of this mechanism have been limited to using—at least partially—the high temperature approximation, in which Boltzmann factors are expanded linearly. However, the high nuclear spin polarization required and obtained for these applications does not justify such approximations.

This article extends the description of thermal mixing beyond the high temperature approximation, so Boltzmann factors are not expanded. It applies for DNP in samples doped with paramagnetic centres, for which the electron spin resonance spectrum is mainly inhomogeneously broadened by  $g$ -value anisotropy. It verifies Provotorov's hypothesis that fast spectral diffusion leads to a density matrix containing two inverse spin temperatures: the inverse electron Zeeman temperature and the inverse electron non-Zeeman temperature, while thermal mixing equalizes the nuclear Zeeman temperature and the electron non-Zeeman temperature. Equations are derived for the evolution of these temperatures and the energy flows between the spins and the lattice. Solutions are given for DNP of proton spins in samples doped with the radical TEMPO.

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## 1. Introduction

Dynamic Nuclear Polarization (DNP) is a powerful tool to obtain high nuclear spin polarization. During several decades the main drive for its development was its application in polarized targets for the study of the role of spin in nuclear and particle interactions—for a review see [1]. Then its potential to enhance Nuclear Magnetic Resonance (NMR) signals became a driving force to develop its application in different fields of NMR [2]. In the past decade DNP enabled a huge increase in contrast in Magnetic Resonance Imaging (MRI) [3,4] which opened the way to clinical applications [5].

In DNP one polarizes nuclear spins in an insulating solid. This solid is doped with radicals or paramagnetic ions providing unpaired electron spins. These electron spins are polarized by cooling to about 1 K and applying a magnetic field of several tesla. Then the electron spin polarization is transferred to the surrounding nuclear spins by means of a CW microwave field. For reviews of the theoretical background see [6–10].

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Two mechanisms have been identified for the polarization transfer. In the solid effect the microwave field directly induces simultaneous transitions of electron spins and nuclear spins transferring polarization of the electron spins to the nuclear spins. In the other mechanism the microwave field first reduces the polarization of some electron spins, so different electron spins may have different polarization. Next, the mutual interaction between the electron spins and the hyperfine or super-hyperfine interaction between the electron spins and the nuclear spins combine to transfer such differences of polarization to the nuclear spins. If the electron spin system is in a local equilibrium this process is known as thermal mixing, otherwise as the cross effect.

This article concerns thermal mixing, so we assume that the mutual interaction between the electron spins,  $\mathcal{H}_{SS}$ , transfers electron spin polarization so fast across the whole electron spin resonance (ESR) spectrum, that a local equilibrium is established in the electron spin system. Thus far almost all theoretical treatments of thermal mixing involve the high temperature approximation in which Boltzmann factors are expanded linearly. Though several authors treated magnetic resonance beyond this approximation [11–13], in only two cases this work led to a model from which DNP results can be predicted. One case is Borghini's model, but this model is restricted to the limit of a strong microwave field and

treats the stationary state only [14]. Jannin et al. extended Borghini's model to weaker microwave fields [15], but still restricted their treatment to fast thermal mixing and the stationary state. The situation is unfortunate, because many applications require such high nuclear spin polarization, that the high temperature approximation cannot be justified. This paper extends the theory of thermal mixing to low spin temperature without imposing the above mentioned restrictions.

Such an extension poses several challenges. To explain them we refer to Fig. 1. It shows the usual division of the spin system in three reservoirs: the electron Zeeman reservoir containing the average Zeeman energy of the electron spins, the electron non-Zeeman reservoir containing all other contributions to the energy of the electron spins, and the nuclear Zeeman reservoir containing the nuclear Zeeman energy. In DNP via thermal mixing the microwave field adds energy to the electron spins. The mutual interaction  $\mathcal{H}_{SS}$  between the electron spins distributes this energy in such a way over the electron Zeeman reservoir and the electron non-Zeeman reservoir that the electron Zeeman reservoir heats up and the electron non-Zeeman reservoir cools down. The coupling  $\mathcal{H}_{SI}$  between electron and nuclear spins combines with  $\mathcal{H}_{SS}$  to cool the nuclear Zeeman reservoir as well. Thus, the nuclear spins are polarized.

The first challenge is to describe the state of the electron Zeeman and electron non-Zeeman reservoirs. Provotorov proposed that only two parameters are needed when the magnetic resonance spectrum is homogeneously broadened [16]. This assumption was subsequently extended to inhomogeneous ESR spectra, in which spectral diffusion is fast—for early reviews, see [6–8]. These two parameters are generally denoted as the inverse electron Zeeman temperature  $\alpha = \hbar/k_B T_Z$  and the inverse electron non-Zeeman temperature  $\beta_{NZ} = \hbar/k_B T_{NZ}$ . Here  $\hbar$  is Planck's constant and  $k_B$  Boltzmann's constant. Abundant experimental support is available for homogeneously broadened magnetic resonance spectra—for a review see [9]. But this hypothesis still needs theoretical proof for inhomogeneous ESR spectra, in which spectral diffusion is fast.

The second challenge is to construct and solve equations for the evolution of  $\alpha$  and  $\beta_{NZ}$  when a microwave field is applied and electron spin-lattice relaxation occurs. Finally, one has to show that  $\mathcal{H}_{SI}$  and  $\mathcal{H}_{SS}$  equalize the inverse nuclear Zeeman temperature  $\beta_I = \hbar/k_B T_I$  and the inverse electron non-Zeeman temperature  $\beta_{NZ}$ . Early experimental proofs were provided at higher temperature [17] as well as at low temperature [18], and the rate of this process has been studied theoretically in detail [19,7,9]. But it was only recently proven that the fundamental triple spin flips—introduced by Kessenikh [20] and causing this process—always tend to equalize these two inverse spin temperatures [10].

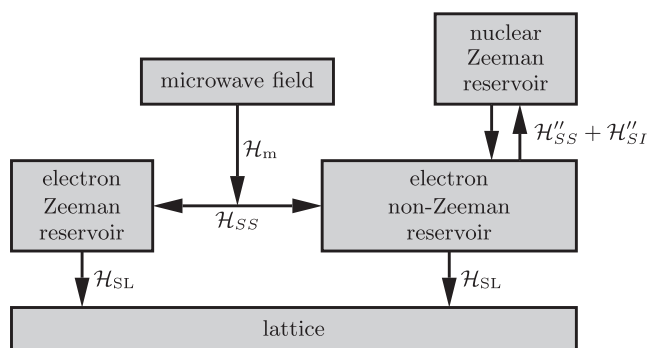


Fig. 1. Schematic diagram of the energy reservoirs and the flows of energy between them.

In the following sections we provide a proof that Provotorov's hypothesis is valid at all temperatures for typical samples used for DNP. The proof from [10] that  $\mathcal{H}_{SI}$  and  $\mathcal{H}_{SS}$  equalize the inverse nuclear Zeeman temperature  $\beta_I = \hbar/k_B T_I$  and the inverse electron non-Zeeman temperature  $\beta_{NZ}$  is reviewed. Next, equations are constructed from which the evolution of the inverse electron Zeeman temperature  $\alpha$  and the inverse electron non-Zeeman temperature  $\beta_{NZ}$  can be solved. To illustrate the results, these equations are subsequently applied to proton spin polarization in glasses doped with TEMPO. Finally the range of applicability of the theory is explored by applying it to two previously published experimental results.

## 2. Energy reservoirs

We start reviewing the spin system. We consider an insulating solid containing  $N_I$  nuclear spins  $I^k = I = \frac{1}{2}$  subjected to a static magnetic field along the z-axis of the laboratory frame of reference. The aim of DNP is to increase their polarization

$$P_I^k = \frac{1}{I} \frac{\text{Tr}\{\rho I_z^k\}}{\text{Tr}\{\rho\}}, \quad (1)$$

in which  $\rho$  is the density matrix. For this purpose this solid is doped with  $N_S$  electron spins  $S^i = S = \frac{1}{2}$  and the temperature is lowered in order to increase their polarization

$$P_S^i = -\frac{1}{S} \frac{\text{Tr}\{\rho S_z^i\}}{\text{Tr}\{\rho\}}. \quad (2)$$

Next a microwave field is applied to transfer this polarization to the nuclear spins.

We describe the mechanism of thermal mixing for this polarization transfer with the Hamiltonian

$$\mathcal{H} = \mathcal{Z}_S + \mathcal{Z}_I + \mathcal{H}_m + \mathcal{H}_{SS} + \mathcal{H}_{SI} + \mathcal{H}_{II} + \mathcal{H}_{SL} + \mathcal{H}_L. \quad (3)$$

Here

$$\mathcal{Z}_S = \hbar \sum_{i=1}^{N_S} \omega_{0S}^i S_z^i \quad (4)$$

and

$$\mathcal{Z}_I = -\hbar \omega_{0I} \sum_{k=1}^{N_I} I_z^k \quad (5)$$

are the Zeeman interactions of the electron and nuclear spins with the externally applied magnetic field. We allow for anisotropy of the g-tensor leading to different Zeeman splittings  $\hbar\omega_{0S}^i$  for different electron spins. The difference in sign between (4) and (5) reflects that in most samples used in DNP the gyromagnetic ratio of electron spins is negative, while that of nuclear spins is positive. For the same reason the signs in (1) and (2) are opposite.

In the remainder of the Hamiltonian (3),  $\mathcal{H}_m$  represents the interaction of the electron spins with the microwave field,  $\mathcal{H}_{SS}$  the mutual interaction between the electron spins and  $\mathcal{H}_{II}$  the mutual interaction between the nuclear spins. Furthermore  $\mathcal{H}_{SI}$  contains the hyperfine coupling—which is partly a contact interaction and partly of dipolar origin—of the electron spins with so-called core or local nuclear spins near the electron spins and the super-hyperfine interaction—which is purely dipolar—between the electron spins and so-called bulk nuclear spins further away. Finally  $\mathcal{H}_L$  represents the lattice vibrations, while the coupling  $\mathcal{H}_{SL}$  between the electron spins and the lattice causes electron spin-lattice relaxation.

We consider the matrix representation of the spin part of the Hamiltonian on a basis of eigenstates

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