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Dynamic nuclear polarization via the cross effect and thermal mixing: A. The role of triple spin flips

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ABSTRACT

In dynamic nuclear polarization (DNP) via the cross effect (CE) and thermal mixing (TM) a microwave field first reduces the polarization of some electron spins, so the electron spin system deviates from thermal equilibrium with the lattice. Next, the mutual interactions combine with their interaction with the nuclear spins to transform this deviation into nuclear spin polarization.

Two approaches were introduced to describe the latter process. The fluctuating field approach considers the electron spins to fluctuate between their up and down states due to their mutual interactions. This results in a classical fluctuating field at the position of the nuclear spins, and the component of this field at the NMR frequency induces flips of the nuclear spins. The scrambled states approach considers the electron and nuclear spin states to be mixed by the hyperfine and super-hyperfine interaction. Next the mutual interaction between the electron spins induces transitions between these mixed states and thus flips nuclear spins. Some authors considered the fluctuating field approach and the scrambled states approach to be just two equivalent methods to describe exactly the same process. Other authors considered the two approaches to describe two separate processes, the former exchanging electron interaction energy, the latter transferring differences of electron spin polarization to the nuclear spins.

The present work introduces a generalized approach that first calculates the mixing of electron spin states exactly. Next it considers the hyperfine or super-hyperfine interaction to induce transitions involving these mixed states and the nuclear spin states. It is found that the scrambled states approach and the fluctuating field approach are neither fully equivalent, nor completely independent processes, but rather represent two distinct limits of a single process. The former corresponding to very weak mutual interactions between electron spins and the latter to very strong mutual interactions. It extends the treatment to the whole range of mutual interactions and shows that this single process simultaneously exchanges electron Zeeman energy and electron interaction energy with the nuclear spins. Expressions for these two flows as a function of the strength of the mutual interaction are derived.

1. Introduction

Dynamic Nuclear Polarization (DNP) is a powerful tool to obtain high nuclear spin polarization. While at first its development was driven by studies of the role of spin in nuclear and particle physics—for a review see [1], more recently its potential to enhance nuclear magnetic resonance (NMR) signals [2] and contrast in magnetic resonance imaging (MRI) [3–5] is the driving force for its development.

These applications use DNP to polarize nuclear spins in insulating solids—mostly glasses—doped with an agent providing unpaired electron spins. The latter 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].

Two families of mechanisms have been identified for the polarization transfer. In the solid effect (SE) the microwave field combines with the hyperfine and super-hyperfine interaction between electron and nuclear spins to transfer electron spin polarization directly to the nuclear spins. In the other family of mechanisms—known as the cross effect (CE) and thermal mixing (TM)—the nuclear spins are polarized in a three step process. In the first step the microwave field reduces the polarization of some electron spins. In the second step the mutual interaction between electron

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spins induces spectral diffusion, a process in which the reduction of electron spin polarization is spread over the other electron spins. Both steps change the electron interaction energy—i.e. the expectation value of the their mutual interactions [11,12]. In the third and final step the mutual interaction between the electron spins and their hyperfine and super-hyperfine interaction with the nuclear spins combine to transform the modified state of the electron spins into nuclear spin polarization.

Two approaches were introduced to describe this final step. The fluctuating field approach was introduced by Buishvili [13], Provotorov and Kozhusner [14,15] and subsequently further developed by Goldman [16]. In this approach the electron spins are considered to fluctuate between their up and down states due to their mutual interactions. This results in a classical fluctuating field at the position of the nuclear spins, and the component of this field at the NMR frequency ω_{0I} induces flips of the nuclear spins. This approach considers the nuclear spin polarization to be due to an exchange of electron interaction energy and nuclear Zeeman energy.

The scrambled states approach was introduced by Kessenikh [17] and further developed by Hwang and Hill [18] and more recently by e.g. Vega and co-workers [19]. This approach considers the electron and nuclear spin states to be mixed by the hyperfine and super-hyperfine interaction between electron and nuclear spins. Next the mutual interaction between the electron spins induces transitions between these mixed states and thus flips nuclear spins. This approach considers the nuclear spin polarization to be due to a transfer of differences between electron spin polarizations.

Often the fluctuating field approach and the scrambled states approach have been considered as just two alternative methods to describe exactly the same process and leading to the same result. Abragam and Goldman for instance show that these two approaches lead to exactly the same rate for direct relaxation of nuclear spins, in which the electron spin-lattice interaction combines with the hyperfine and super-hyperfine interaction between electron and nuclear spins to flip both types of spin simultaneously [9]. This has induced several authors—e.g. [6,9]—to consider only one of these two approaches for the description of this family of mechanisms for DNP. Other authors—e.g. [20]—considered the two approaches to describe distinct processes that can be treated separately. In still another case [21] the two approaches were considered as extreme cases of a unified treatment, but that work did not follow through in determining the flows of energy in the spin system.

The present work introduces a generalization of an alternative scrambled states approach, which was recently introduced in [10], Chapter 8. This alternative approach considers the electron spin states to be mixed by the mutual interaction between electron spins. Next the hyperfine and super-hyperfine interaction between the electron and nuclear spins induce transitions involving these mixed states and the nuclear spin states. The generalization to be presented here, calculates the mixing of electron spin states exactly, so the whole spectrum of the mutual interactions is taken into account. This procedure is similar to the treatment of pulsed DNP techniques like nuclear orientation via electron spin locking (NOVEL) and the integrated solid effect (ISE). Then one first determines the exact eigenstates of electron spins interacting with a microwave field and next studies transitions involving these exact eigenstates and the nuclear spin states [22,23]. The details of this similarity are discussed in Appendix A.

It is found that the scrambled states approach and the fluctuating field approach are neither fully equivalent, nor completely independent processes, but rather represent two distinct limits of a single process. The former corresponding to very weak mutual interactions between electron spins and the latter to very strong mutual interactions. The generalization presented here extends the treatment to the whole range of mutual interactions and shows that in general this single process generates simultaneously a flow of electron Zeeman energy and a flow of electron interaction energy to or from the nuclear spins. In this article we denote the former flow as the cross effect (CE) and the latter flow as thermal mixing (TM).

This article analyses the fundamental transition in this single process—the be denoted in this article as a triple spin flip—using a model system consisting of just two electron spins and a single nuclear spin embedded in a glass—and derives rate equations for the two simultaneous flows of energy. The following article [24] extends this treatment to a model system consisting of N_S electron spins and N_I equivalent nuclear spins. In that article the electron spin system is next modelled as in Provotorov's treatments of magnetic resonance saturation and cross-relaxation [11,12]. This enables the inclusion of the effects of the microwave field, spectral diffusion and electron spin-lattice relaxation, so a complete description of DNP can be obtained, albeit in the high temperature approximation. Notice however, that the treatment of triple spin flips presented in this article and the next, is not restricted to the high temperature approximation, and that extensions beyond the high temperature approximation using the models for magnetic resonance saturation and spectral diffusion presented in [25,26] are feasible.

2. Model system for triple spin flips

We consider DNP in a glass containing nuclear spins $I = \frac{1}{2}$ and doped with randomly distributed and oriented radicals, that provide unpaired electron spins $S = \frac{1}{2}$ with anisotropic g-tensors. As described in the introduction, a static magnetic field is applied to polarize the electron spins and a microwave field is used to reduce the polarization of some electron spins, so different electron spins may have different polarization. Next triple spin flips, involving two electron spins and one nuclear spin, transfer these differences of polarization to the nuclear spins. Many issues involving such triple spin flips can be treated considering a minimum sub-system consisting of just two electron spins S and S' and a single nuclear spin I interacting with S. Therefore this article concentrates on such a minimum sub-system and the extension to more spins is postponed to the following article [24].

We describe this minimum sub-system with the Hamiltonian

$$\mathcal{H} = \mathcal{H}_S + \mathcal{Z}_I + \mathcal{V}, \tag{1}$$

$$\mathcal{H}_S = \omega_{0S}S_z + \omega'_{0S}S'_z + D_{zz}S_zS'_z + \frac{1}{2}D_{+-}(S_+S'_- + S_-S'_+), \tag{2}$$

$$\mathcal{Z}_I = -\omega_{0I}I_z, \tag{3}$$

$$\mathcal{V} = \frac{1}{2}S_z(A_{z-}I_+ + A_{z+}I_-). \tag{4}$$

Here the z-axis of the laboratory frame of reference is chosen along the externally applied magnetic field, and $S_\pm = S_x \pm iS_y, S'_\pm = S'_x \pm iS'_y, I_\pm = I_x \pm iI_y$. Also Planck's constant $\hbar$ is skipped in the Hamiltonian, so the energy is expressed in frequency units. In the electron spin part $\mathcal{H}_S$ of this Hamiltonian the first two terms represent the Zeeman interaction of the electron spins with the externally applied magnetic field. Notice that the Zeeman splittings ω_{0S} and ω'_{0S} are generally different because of anisotropy of the g-tensor. The third and fourth term in $\mathcal{H}_S$ represent the mutual interaction between the electron spins needed to induce triple spin flips and is truncated [27]. For DNP the concentration of electron spins is generally low—typically $1 \cdot 10^{19}$ to $4 \cdot 10^{19}\,\mathrm{cm}^{-1}$ (16–66 mM)—and this mutual interaction between electron spins is almost purely dipolar. Then $D_{zz} = 2D_{+-}$ and real[1].

The following term in the Hamiltonian (1) represents the Zeeman interaction of the nuclear spin with the externally applied magnetic field and the last term the hyperfine or super-hyperfine interaction between the electron spin S and the nuclear spin I. Notice that all terms in the latter interaction are skipped except those inducing nuclear spin flips. Thus we ignore shifts of the energy levels due to the interaction between the electron spins and the nuclear spins surrounding them. This is not a trivial simplification. As was pointed out in Abragam and Goldman's [9] treatment of Borghini's model [28], this can only be justified when the ESR lineshape is mainly broadened by g-tensor anisotropy—as is fortunately mostly the case for paramagnetic centres in glasses. Otherwise shifts of the energy levels of the electron spins due to polarization of the local nuclear spins near the electron spins need to be accounted for.

In what follows we skip the term $D_{zz}S_zS'_z$ in the mutual interaction between the electron spins, as its expectation value does not change in triple spin flips, nor does it induce transitions. We also ignore the interaction of the two electron spins with all other electron spins in the sample. For the dynamics of the electron spins this implies that we ignore transitions involving more than two electron spins. For the statics of the electron spin system it implies that we ignore level shifts due to such interactions.

Our aim is to study the flows of energy in the spin system. For this purpose we derive equations for the evolution of the polarization

$$P_I = \frac{1}{I}\frac{\mathrm{Tr}\{\rho I_z\}}{\mathrm{Tr}\{\rho\}} \tag{5}$$

of the nuclear spin and the polarization

$$P_S = -\frac{1}{S}\frac{\mathrm{Tr}\{\rho S_z\}}{\mathrm{Tr}\{\rho\}} \quad \text{and} \quad P'_S = -\frac{1}{S}\frac{\mathrm{Tr}\{\rho S'_z\}}{\mathrm{Tr}\{\rho\}} \tag{6}$$

of the two electron spins in time. Here ρ is the density matrix. As mentioned in the introduction, instead of the fluctuating field approach or the scrambled states approach we use an extension of the alternative scrambled states approach introduced in [10]. This extension first determines the mixing of electron spin states by their mutual interaction exactly. Next it uses first order perturbation theory to treat the transitions induced by the interaction between one of the electron spins and the nuclear spin. Thus it considers

$$\mathcal{H}_0 = \mathcal{H}_S + \mathcal{Z}_I \tag{7}$$

as the unperturbed Hamiltonian and $\mathcal{V}$ as the perturbation.

To obtain the evolution of P_I, P_S and P'_S in time, we need to solve the evolution of the density matrix ρ from the Liouville equation. We use the first order perturbation expansion developed by Zwanzig [29]. In this expansion we first determine the eigenstates $|p\rangle$ and energy levels ω_p of the unperturbed Hamiltonian $\mathcal{H}_0$. Next we consider the density matrix ρ on a basis of these eigenstates. We assume that transverse relaxation keeps all non-diagonal elements $\rho_{pq} = \langle p|\rho|q\rangle$ of the density matrix near zero at all times. Thus this treatment excludes all coherent effects. We also exclude longitudinal relaxation. Then the Liouville equation reduces to a set of rate equations for the diagonal elements $\rho_{pp} = \langle p|\rho|p\rangle$ of the density matrix:

$$\frac{\partial \rho_{pp}}{\partial t} = -\sum_q W_{pq}\left(\rho_{pp} - \rho_{qq}\right), \tag{8}$$

in which the transition rates W_{pq} are given by Fermi's golden rule. In the next two sections we first derive and discuss an expression for the transition rates W_{pq}. Subsequently we construct such rate equations and use these to obtain the evolution in time of P_I, P_S and P'_S and to determine the flows of energy.

3. Transition rates

We determine the rate of triple spin flips, i.e. the rate at which the perturbation $\mathcal{V}$ induces transitions between the eigenstates of the unperturbed Hamiltonian $\mathcal{H}_0$. First we need to diagonalize the latter. The nuclear spin part $\mathcal{Z}_I$ is diagonal on a basis of eigenstates $|m_I\rangle$ of I_z and needs no further work. So we concentrate on the electron spin part $\mathcal{H}_S$ and consider its matrix representation on a basis of eigenstates $|m_S m'_S\rangle$ of S_z and S'_z. The mutual interaction between the two electron spins only mixes the states $|+\frac{1}{2}-\frac{1}{2}\rangle$ and $|-\frac{1}{2}+\frac{1}{2}\rangle$, so we only need to diagonalize the 2×2 sub-matrix:

$$\frac{1}{2}\begin{pmatrix} \omega_{0S} - \omega'_{0S} & D_{+-} \\ D_{+-} & -(\omega_{0S} - \omega'_{0S}) \end{pmatrix} \tag{9}$$

on the basis of these two states.

Now notice that this sub-matrix also represents the Hamiltonian

$$\mathcal{H}_J = (\omega_{0S} - \omega'_{0S})J_z + D_{+-}J_x \tag{10}$$

of a fictitious spin $J = \frac{1}{2}$ subjected to a frequency vector $\boldsymbol{\omega}_J$ with components

$$\begin{aligned} \omega_J^x &= D_{+-}, \\ \omega_J^y &= 0, \\ \omega_J^z &= \omega_{0S} - \omega'_{0S}. \end{aligned} \tag{11}$$

As seen in Fig. 1, this frequency vector has a length

$$\omega_J = \sqrt{\left(\omega_{0S} - \omega'_{0S}\right)^2 + D_{+-}^2}, \tag{12}$$

and is tilted about the y-axis through an angle θ defined by

$$\sin\theta = \frac{D_{+-}}{\omega_J}, \qquad \cos\theta = \frac{\omega_{0S} - \omega'_{0S}}{\omega_J}. \tag{13}$$

So we can write the effective Hamiltonian (10) also as

$$\mathcal{H}_J = \omega_J(J_z\cos\theta + J_x\sin\theta). \tag{14}$$

We now tilt our frame of reference through the angle θ about the y-axis, so the new $\tilde{z}$-axis is parallel to the effective frequency vector. In this new frame of reference the x and z-components of the electron spin transform to

$$\begin{aligned} J_{\tilde{x}} &= J_x\cos\theta - J_z\sin\theta, \\ J_{\tilde{z}} &= J_x\sin\theta + J_z\cos\theta, \\ J_{\tilde{y}} &= J_y. \end{aligned} \tag{15}$$

So inversely,

$$\begin{aligned} J_x &= J_{\tilde{x}}\cos\theta + J_{\tilde{z}}\sin\theta, \\ J_z &= J_{\tilde{z}}\cos\theta - J_{\tilde{x}}\sin\theta, \\ J_y &= J_{\tilde{y}}. \end{aligned} \tag{16}$$

As a result of this transformation the effective Hamiltonian (14) simplifies to

$$\widetilde{\mathcal{H}}_J = \omega_J J_{\tilde{z}}. \tag{17}$$

[1] Notice that D_{+-} is chosen to be a factor two smaller than e.g. in [10]. This enables the expressions in this article and the next [24] to be written more concisely.

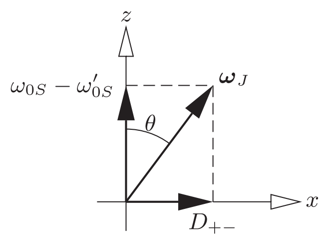

Fig. 1. The effective frequency vector.

As mentioned above, triple spin flips only involve the basis states $|m_S m'_S\rangle = |+\frac{1}{2}-\frac{1}{2}\rangle$ and $|-\frac{1}{2}+\frac{1}{2}\rangle$. To describe them, we can therefore use a Hamiltonian consisting of the effective Hamiltonian (10) extended with the nuclear spin parts (3) and (4) of the Hamiltonian (1). After applying the transformation (15) and inserting $J_\pm = J_{\tilde{x}} \pm iJ_{\tilde{y}}$, this extended effective Hamiltonian is given by

$$\begin{aligned}\widetilde{\mathcal{H}} = \;& \omega_J J_{\tilde{z}} - \omega_{0I} I_z + \tfrac{1}{2} J_{\tilde{z}} (A_{z-} I_+ + A_{z+} I_-) \cos\theta \\ & - \tfrac{1}{4}\left(A_{z-} J_+ I_- + A_{z+} J_- I_+\right) \sin\theta \\ & - \tfrac{1}{4}\left(A_{z-} J_+ I_+ + A_{z+} J_- I_-\right) \sin\theta.\end{aligned} \tag{18}$$

Here the first term has the shape of a Zeeman interaction of the fictitious spin J, and the second represents the real Zeeman interaction of the nuclear spin I. On a basis of eigenstates $|m_J m_I\rangle$ of $J_{\tilde{z}}$ and I_z the remaining terms are non-diagonal. The first of these induces pure nuclear spin flips

$$|m_I\rangle = \left|+\frac{1}{2}\right\rangle \leftrightarrow \left|-\frac{1}{2}\right\rangle, \tag{19}$$

requiring energy $\pm\omega_{0I}$. The remaining two terms induce flip-flop and flip-flip transitions

$$|m_J m_I\rangle = \left|+\frac{1}{2}-\frac{1}{2}\right\rangle \leftrightarrow \left|-\frac{1}{2}+\frac{1}{2}\right\rangle \tag{20}$$

and

$$|m_J m_I\rangle = \left|+\frac{1}{2}+\frac{1}{2}\right\rangle \leftrightarrow \left|-\frac{1}{2}-\frac{1}{2}\right\rangle \tag{21}$$

between the effective electron spin J and the nuclear spin I, the former requiring energy $\pm(\omega_J + \omega_{0I})$ and the latter energy $\pm(\omega_J - \omega_{0I})$. Notice that the eigenstates $|m_J\rangle$ of $J_{\tilde{z}}$ are linear combinations of the basis states $|m_S m'_S\rangle = |+\frac{1}{2}-\frac{1}{2}\rangle$ and $|-\frac{1}{2}+\frac{1}{2}\rangle$. Hence, the transitions (20) and (21) actually involve both electron spins S and S' and the nuclear spin I, i.e. they are just the triple spin flips we are investigating.

As both $\omega_J > 0$ and $\omega_{0I} > 0$, only transitions of the type (21) are allowed in first order. We truncate the effective Hamiltonian (18) and skip the two terms that cannot induce transitions. Then

$$\widetilde{\mathcal{H}} = \omega_J J_{\tilde{z}} - \omega_{0I} I_z - \frac{1}{4}\left(A_{z-} J_+ I_+ + A_{z+} J_- I_-\right) \sin\theta. \tag{22}$$

We now use first order perturbation theory to determine the rate of transitions of the type (21) induced by the remaining non-diagonal term. We find

$$\begin{aligned} W_{SSI} &= \tfrac{\pi}{2}\, |\tfrac{1}{2} A_{z+}|^2 \sin^2\theta\, \delta(\omega_{0I} - \omega_J) \\ &= \tfrac{\pi}{2}\, \frac{|\frac{1}{2}A_{z+}|^2 D_{+-}^2}{\omega_{0I}^2}\, \delta(\omega_{0I} - \omega_J)\end{aligned} \tag{23}$$

for this rate. Here the δ-function represents conservation of energy: the energy released or absorbed by a flip of the fictitious spin J needs to be absorbed or released by the nuclear spin. In other words: in triple spin flips the two electron spins need to provide the energy needed to flip the nuclear spin.

4. Matching conditions

Fig. 2 is a graphical representation of the matching condition

$$\omega_{0I} = \omega_J = \sqrt{\left(\omega_{0S} - \omega'_{0S}\right)^2 + D_{+-}^2} \tag{24}$$

implied by the δ-function

$$\delta(\omega_{0I} - \omega_J) = \delta\left(\omega_{0I} - \sqrt{\left(\omega_{0S} - \omega'_{0S}\right)^2 + D_{+-}^2}\right) \tag{25}$$

in the transition rate (23). As Fig. 1 it plots the difference $\omega_{0S} - \omega'_{0S}$ between the Zeeman splittings of the two electron spins as a function of the strength D_{+-} of their mutual interaction. The matching condition (24) is satisfied on the circle which has radius $|\boldsymbol{\omega}_J| = \omega_{0I}$.

The radicals providing the electron spins are embedded randomly in a glass and as a consequence their relative positions are not correlated with their orientation. This implies that the strength D_{+-} of their mutual interaction is not correlated with their Zeeman splittings ω_{0S} and ω'_{0S}. As a consequence, when considering all pairs of electron spins in a sample, no points on the circle can be excluded or preferred because of a correlation between D_{+-} and $\omega_{0S} - \omega'_{0S}$.

Still, experimental conditions may restrict satisfaction of the matching condition to a few sectors on the circle. For instance, the radicals providing the electron spins are finite in size, so there exists a minimum distance between electron spins and hence a maximum value D_0 of $|D_{+-}|$. When the magnetic field is so high that the NMR frequency ω_{0I} is larger than D_0, the matching condition can only be satisfied in two sectors. When for instance $D_0 = 0.5\,\omega_{0I}$, these are the sectors between A and B and between C and D in Fig. 2.

Notice that for $D_0 \ll \omega_{0I}$ we may approximate $\omega_J \approx |\omega_{0S} - \omega'_{0S}|$. Then the δ-function (25) reduces to

$$\delta(\omega_{0I} - \omega_J) \approx \delta\left(\omega_{0I} - |\omega_{0S} - \omega'_{0S}|\right). \tag{26}$$

As a result the main contribution to the polarization transfer is due to electron spins, for which $\omega_{0I} \approx |\omega_{0S} - \omega'_{0S}|$. As we will see below in more detail, the energy needed to flip the nuclear spin then originates mainly in the Zeeman energy of the two electron spins. This is the regime treated with the scrambled states introduced by Kessenikh and treated in more detail by Hwang and Hill [17,18].

Secondly, the finite extend of the ESR lineshape may limit the difference between the resonance frequencies of the two electron spins to a range $-\Delta_{max} < \omega_{0S} - \omega'_{0S} < \Delta_{max}$. When this lineshape is so narrow that the NMR frequency ω_{0I} is larger than Δ_{max}, the matching condition can again be satisfied in two sectors of the circle only. When e.g. $\Delta_{max} = 0.5\omega_{0I}$, these are the sectors between a and b and between c and d in Fig. 2.

Notice that for $\Delta_{max} \ll \omega_{0I}$ we may approximate $\omega_J \approx |D_{+-}|$. Then the δ-function (25) reduces to

$$\delta(\omega_{0I} - \omega_J) \approx \delta(\omega_{0I} - |D_{+-}|), \tag{27}$$

and the main contribution to polarization transfer to the nuclear spins is due to pairs of electron spins, for which $|D_{+-}| \approx \omega_{0I}$. As we will see below in more detail, the energy needed to flip the nuclear spin then originates mainly in the mutual interactions between the electron spins. This is the regime treated with the fluctuating field approach by Provotorov, Kozhushner and Buishvili [14,15,13] and in more detail by Goldman, Cox and Bouffard [16].

We see that the scrambled states approach and the fluctuating field approach do not represent fully equivalent treatments of triple spin flips, but rather represent two different extreme cases of a more general approach, in which the interaction strength between the electron spins can be varied over a large range.

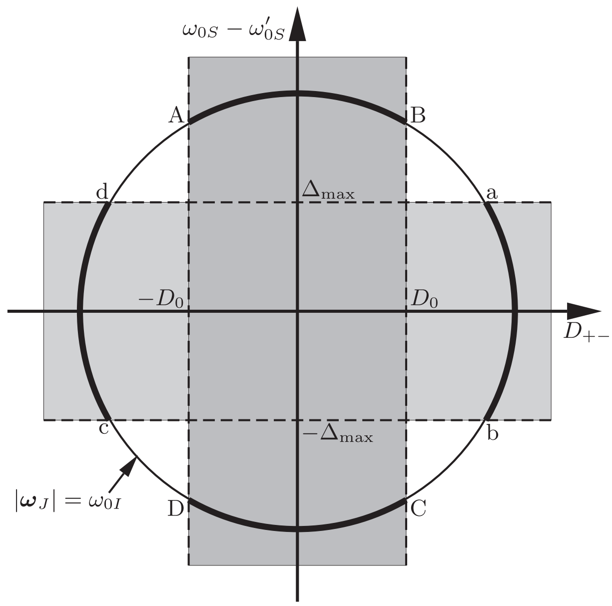

Fig. 2. Matching condition for polarization transfer to the nuclear spins.

Notice that it may occur that both the ESR lineshape is so narrow that $\Delta_{\max} < \omega_{0I}$ and the mutual interaction between electron spins is so weak that $D_0 < \omega_{0I}$. Then triple spin flips cannot conserve energy and hence cannot occur. In such a case DNP and nuclear spin-lattice relaxation is only possible via some other mechanism, for instance the SE.

5. Polarization transfer

We continue with the procedure outlined in Section 2 and construct a rate equation for the evolution of the density matrix describing the state of our minimal system of two electron spins S and S' and a nuclear spin I. Next we rewrite this rate equation into equations for the evolution of the polarization P_S and P'_S of S and S' and the polarization P_I of I. Subsequently, in the following section we rewrite it further into equations for the transport of energy in the spin system.

As discussed in Section 2 we choose $\mathcal{H}_0 = \mathcal{H}_S + \mathcal{Z}_I$ given by (2) and (3) as the unperturbed Hamiltonian and $\mathcal{V}$ given by (4) as the perturbation. The eigenstates

$$\begin{aligned} |m_S m'_S m_I\rangle &= |+\tfrac{1}{2}+\tfrac{1}{2}\mp\tfrac{1}{2}\rangle \\ |m_J m_I\rangle &= |+\tfrac{1}{2}\mp\tfrac{1}{2}\rangle \\ |m_J m_I\rangle &= |-\tfrac{1}{2}\mp\tfrac{1}{2}\rangle \\ |m_S m'_S m_I\rangle &= |-\tfrac{1}{2}-\tfrac{1}{2}\mp\tfrac{1}{2}\rangle \end{aligned} \tag{28}$$

of $\mathcal{H}_0$ were already discussed in Section 3, just as the rate W_{SSI} of transitions between the eigenstates that are induced by $\mathcal{V}$, but we still need to construct the density matrix. As mentioned in Section 2, we assume that fast transverse relaxation keeps the non-diagonal components of the density matrix ρ near zero at all times. Moreover, the unperturbed Hamiltonian does not mix electron spin states and nuclear spin states. As a result the density matrix can be factorized in a diagonal electron spin part

$$\rho_S = \begin{pmatrix} \rho_S^{++} & 0 & 0 & 0 \\ 0 & \rho_J^{+} & 0 & 0 \\ 0 & 0 & \rho_J^{-} & 0 \\ 0 & 0 & 0 & \rho_S^{--} \end{pmatrix} \tag{29}$$

and a diagonal nuclear spin part

$$\rho_I = \begin{pmatrix} \rho_I^{-} & 0 \\ 0 & \rho_I^{+} \end{pmatrix}, \tag{30}$$

the traces of which can be normalized separately:

$$\mathrm{Tr}\{\rho_S\} = \rho_S^{++} + \rho_J^{+} + \rho_J^{-} + \rho_S^{--} = 1 \tag{31}$$

$$\mathrm{Tr}\{\rho_I\} = \rho_I^{+} + \rho_I^{+} = 1. \tag{32}$$

Notice that triple spin flips only involve the states $|m_J m_I\rangle = |+\frac{1}{2}+\frac{1}{2}\rangle$ and $|-\frac{1}{2}-\frac{1}{2}\rangle$. So all diagonal components of the density matrix are constant in time except $\rho_J^+\rho_I^+$ and $\rho_J^-\rho_I^-$. As a result the rate equation

$$\frac{\partial}{\partial t}\left(\rho_J^+\rho_I^+ - \rho_J^-\rho_I^-\right) = -W_{\mathrm{SSI}}\left(\rho_J^+\rho_I^+ - \rho_J^-\rho_I^-\right), \tag{33}$$

suffices to describe the evolution of the diagonal components of the density matrix.

Our next aim is to establish relations between the evolution of the polarization P_S and P'_S of the two electron spins S and S' and the polarization P_I of the nuclear spin I. To obtain these relations we express these polarizations in the components of the density matrix and rewrite the left hand side of the rate Eq. (33) in terms of the evolution of these polarizations. Upon insertion of the normalization (32), the polarization (5) of the nuclear spin becomes

$$P_I = \frac{1}{I}\frac{\mathrm{Tr}\{\rho_I I_z\}}{\mathrm{Tr}\{\rho_I\}} = \rho_I^+ - \rho_I^-. \tag{34}$$

The polarization (6) of the electron spins does not reduce to such a simple expression, because the states of these two spins are mixed by their mutual interaction. We need to use the full electron spin part (29) of the density matrix describing these mixed states:

$$P_S = -\frac{1}{S}\frac{\mathrm{Tr}\{\rho_S S_z\}}{\mathrm{Tr}\{\rho_S\}} \tag{35}$$

and

$$P'_S = -\frac{1}{S}\frac{\mathrm{Tr}\{\rho_S S'_z\}}{\mathrm{Tr}\{\rho_S\}}. \tag{36}$$

To evaluate these expressions, we need to transform the sub-matrix

$$\rho_J = \begin{pmatrix} \rho_J^{+} & 0 \\ 0 & \rho_J^{-} \end{pmatrix} \tag{37}$$

of ρ_S from a basis of eigenstates of $J_{\tilde z}$ in the tilted frame of reference to a basis of eigenstates $|m_S m'_S\rangle$ of S_z and S'_z in the laboratory frame of reference. This is most easily done by writing this sub-matrix in terms of the components of the fictitious spin J and tilting the frame of reference over an angle $-\theta$ about the y-axis. We introduce the 2×2 unit matrix $\mathbf{1}$ and use the transformation rule (15). Then we find that the sub-matrix (37) transforms to

$$\begin{aligned} \rho_J &= \tfrac{1}{2}\left(\rho_J^+ + \rho_J^-\right)\mathbf{1} + \left(\rho_J^+ - \rho_J^-\right)J_{\tilde z} \\ &= \tfrac{1}{2}\left(\rho_J^+ + \rho_J^-\right)\mathbf{1} + \left(\rho_J^+ - \rho_J^-\right)\left(J_z\cos\theta + J_x\sin\theta\right) \\ &= \tfrac{1}{2}\begin{pmatrix} \rho_S^{+-} & \rho_S^{\perp} \\ \rho_S^{\perp} & \rho_S^{-+} \end{pmatrix}, \end{aligned} \tag{38}$$

in which

$$\rho_S^{\pm\mp} = \frac{1}{2}\left(\rho_J^+ + \rho_J^-\right) \pm \frac{1}{2}\left(\rho_J^+ - \rho_J^-\right)\cos\theta, \tag{39}$$

$$\rho_S^{\perp} = \frac{1}{2}\left(\rho_J^+ - \rho_J^-\right)\sin\theta. \tag{40}$$

Thus, after transforming to a basis of eigenstates $|m_S m'_S\rangle$ of S_z and S'_z, the electron spin part of the density matrix is given by

$$\rho_S = \begin{pmatrix} \rho_S^{++} & 0 & 0 & 0 \\ 0 & \rho_S^{+-} & \rho_S^{\perp} & 0 \\ 0 & \rho_S^{\perp} & \rho_S^{-+} & 0 \\ 0 & 0 & 0 & \rho_S^{--} \end{pmatrix}, \tag{41}$$

Upon insertion of the normalization (31), it is then immediately found that

$$P_S = -\left(\rho_S^{++} + \left(\rho_J^{+} - \rho_J^{-}\right)\cos\theta - \rho_S^{--}\right) \tag{42}$$

and

$$P'_S = -\left(\rho_S^{++} - \left(\rho_J^{+} - \rho_J^{-}\right)\cos\theta - \rho_S^{--}\right). \tag{43}$$

Notice that

$$P_S + P'_S = -2\left(\rho_S^{++} - \rho_S^{--}\right) \tag{44}$$

and

$$P_S - P'_S = -2\left(\rho_J^{+} - \rho_J^{-}\right)\cos\theta. \tag{45}$$

We can now rewrite the left hand side of the rate Eq. (33) in terms of the nuclear spin polarization P_I and the electron spin polarizations P_S and P'_S. Recall that all diagonal components of the density matrix remain constant in time except $\rho_J^+\rho_I^+$ and $\rho_J^-\rho_I^-$. Moreover, the density matrix is normalized in such a way that the traces (31) and (32) are equal to one and hence conserved in time. As a result the left hand side of (33) can be rewritten as

$$\begin{aligned} \tfrac{\partial}{\partial t}\left(\rho_J^+\rho_I^+ - \rho_J^-\rho_I^-\right) &= \tfrac{\partial}{\partial t}\left(\rho_S^{++}\rho_I^+ - \rho_S^{++}\rho_I^- + \rho_J^+\rho_I^+ - \rho_J^+\rho_I^-\right. \\ &\qquad \left. + \rho_J^-\rho_I^+ - \rho_J^-\rho_I^- + \rho_S^{--}\rho_I^+ - \rho_S^{--}\rho_I^-\right) \\ &= \tfrac{\partial}{\partial t}\left(\rho_S^{++} + \rho_J^+ + \rho_J^- + \rho_S^{--}\right)\left(\rho_I^+ - \rho_I^-\right) \\ &= \tfrac{\partial}{\partial t}\left(\rho_I^+ - \rho_I^-\right) = \tfrac{\partial P_I}{\partial t}, \end{aligned} \tag{46}$$

as well as

$$\begin{aligned} \tfrac{\partial}{\partial t}\left(\rho_J^+\rho_I^+ - \rho_J^-\rho_I^-\right) &= \tfrac{\partial}{\partial t}\left(\rho_S^{++}\rho_I^+ + \rho_S^{++}\rho_I^- + \rho_J^+\rho_I^+ + \rho_J^+\rho_I^-\right. \\ &\qquad \left. - \rho_J^-\rho_I^+ - \rho_J^-\rho_I^- - \rho_S^{--}\rho_I^+ - \rho_S^{--}\rho_I^-\right) \\ &= \tfrac{\partial}{\partial t}\left(\rho_S^{++} + \rho_J^+ - \rho_J^- - \rho_S^{--}\right)\left(\rho_I^+ + \rho_I^-\right) \\ &= \tfrac{\partial}{\partial t}\left(\rho_S^{++} + \rho_J^+ - \rho_J^- - \rho_S^{--}\right), \end{aligned} \tag{47}$$

or

$$\begin{aligned} \tfrac{\partial}{\partial t}\left(\rho_J^+\rho_I^+ - \rho_J^-\rho_I^-\right) &= -\tfrac{\partial}{\partial t}\left(\rho_S^{++}\rho_I^+ + \rho_S^{++}\rho_I^- - \rho_J^+\rho_I^+ - \rho_J^+\rho_I^-\right. \\ &\qquad \left. + \rho_J^-\rho_I^+ + \rho_J^-\rho_I^- - \rho_S^{--}\rho_I^+ - \rho_S^{--}\rho_I^-\right) \\ &= -\tfrac{\partial}{\partial t}\left(\rho_S^{++} - \rho_J^+ + \rho_J^- - \rho_S^{--}\right). \end{aligned} \tag{48}$$

Subtraction of the latter two equations and subsequent insertion of (44) yields

$$\frac{\partial P_S}{\partial t} = -\frac{\partial P'_S}{\partial t}, \tag{49}$$

so the total electron spin polarization is conserved. On the other hand addition and subsequent insertion of (45) gives

$$\begin{aligned} \frac{\partial}{\partial t}\left(\rho_J^+\rho_I^+ - \rho_J^-\rho_I^-\right) &= \frac{\partial}{\partial t}\left(\rho_J^+ - \rho_J^-\right) \\ &= -\frac{1}{2\cos\theta}\frac{\partial}{\partial t}\left(P_S - P'_S\right). \end{aligned} \tag{50}$$

As a result, upon insertion of (46),

$$\cos\theta\,\frac{\partial P_I}{\partial t} = -\frac{1}{2}\frac{\partial}{\partial t}\left(P_S - P'_S\right) = -\frac{\partial P_S}{\partial t} = \frac{\partial P'_S}{\partial t}. \tag{51}$$

In the limit of small mutual interaction between the two electrons spins—so $D_{+-} \ll \omega_{0I}$ and $\cos\theta \approx 1$—the latter relation describes a process in which the difference between the polarizations of the two electron spins is transferred to the nuclear spin. Thus these relations describe triple spin flips as a flip-flop transitions between the two electron spins combined with a flip of the nuclear spin. But when the interaction between the two electron spins is larger, this simple picture does not hold any more. In the limit $D_{+-} \to \omega_{0I}$ and $\theta \to \pi/2$, so $\cos\theta \to 0$, the nuclear spin polarization may evolve substantially, while neither the total polarization of the two electron spins nor the difference between their polarization change. It is seen that describing triple spin flips in terms of a transfer of electron spin polarization to the nuclear spin is not adequate. It is better to describe them in terms of a transfer of energy between the electron spins and the nuclear spin. This is done in the next section.

Notice, however, that addition of (47) and (48) and subsequent insertion of (46) also yields

$$\frac{\partial}{\partial t}\left(\rho_J^+ - \rho_J^-\right) = \frac{\partial}{\partial t}\left(\rho_I^+ - \rho_I^-\right) = \frac{\partial P_I}{\partial t}. \tag{52}$$

So triple spin flips can always be interpreted as a flip-flip transition between the fictitious spin J and the nuclear spin, resulting in the transfer of the unnormalized polarization

$$P_J = -\frac{1}{J}\,\mathrm{Tr}\left\{\rho_J J_{\tilde{z}}\right\} = -\left(\rho_J^+ - \rho_J^-\right) \tag{53}$$

of the former in the tilted frame of reference to the latter in the laboratory frame of reference.

6. Energy transfer

We follow Provotorov [11,12] to divide the energy of our three spins into four reservoirs as shown in Fig. 3. The nuclear Zeeman reservoir contains the nuclear Zeeman energy

$$U_I = \frac{\mathrm{Tr}\{\rho_I \mathcal{Z}_I\}}{\mathrm{Tr}\{\rho_I\}} = -\frac{1}{2}\omega_{0I}P_I, \tag{54}$$

where we insert (3) for $\mathcal{Z}_I$. The two electron Zeeman reservoirs contain the Zeeman energy

$$U_Z = \omega_{0S}\,\frac{\mathrm{Tr}\{\rho_S S_z\}}{\mathrm{Tr}\{\rho_S\}} = -\frac{1}{2}\omega_{0S}P_S \tag{55}$$

and

$$U'_Z = \omega'_{0S}\,\frac{\mathrm{Tr}\{\rho_S S'_z\}}{\mathrm{Tr}\{\rho_S\}} = -\frac{1}{2}\omega'_{0S}P'_S \tag{56}$$

of the two electron spins. A third reservoir contains the remaining energy

$$U_{SS} = U_S - U_Z - U'_Z \tag{57}$$

of the electron spins. Here

$$U_S = \frac{\mathrm{Tr}\{\rho_S \mathcal{H}_S\}}{\mathrm{Tr}\{\rho_S\}} \tag{58}$$

is the total energy of the electron spins. In our model consisting of two interacting electron spins and one nuclear spin described by the Hamiltonian (1), this reservoir only contains the energy of the mutual interaction between the two electron spins, and we will denote it as the electron interaction reservoir containing the electron interaction energy U_{SS}. Notice however, that in extensions of this model to more spins and more interactions this reservoir may contain other types of energy as well [7,9]. Then it may be more appropriate to call it the electron non-Zeeman reservoir.

Before continuing we furthermore recall that we skipped the term $D_{zz}S_zS'_z$ in the mutual interaction between the two electron

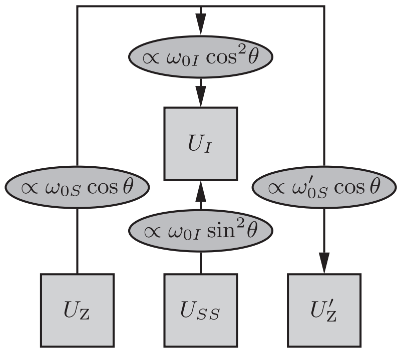

Fig. 3. Energy flows.

spins. Thus we ignore its contribution to the total energy U_S and hence to the electron interaction energy U_{SS}. However, its expectation value is conserved in triple spin flips, so we can still determine the energy flows between the various energy reservoirs without taking this extra term into account.

We derive an expression for the total energy U_S of the two electron spins and deduce the electron interaction energy U_{SS} from it. Our expression (58) for U_S is most easily evaluated using the basis states (28). On this basis the matrix representation of $\mathcal{H}_S$ is diagonal with energy levels

$$\begin{array}{rcll} & \text{state} & & \text{energy} \\ |m_S m'_S\rangle &=& \left|+\tfrac{1}{2}+\tfrac{1}{2}\right\rangle & +\tfrac{1}{2}(\omega_{0S}+\omega'_{0S}) \\ |m_J\rangle &=& \left|+\tfrac{1}{2}\right\rangle & +\tfrac{1}{2}\omega_J \\ |m_J\rangle &=& \left|-\tfrac{1}{2}\right\rangle & -\tfrac{1}{2}\omega_J \\ |m_S m'_S\rangle &=& \left|-\tfrac{1}{2}-\tfrac{1}{2}\right\rangle & -\tfrac{1}{2}(\omega_{0S}+\omega'_{0S}) \end{array} \tag{59}$$

Furthermore the density matrix is given by (29) and normalized by (31). Thus we find for the total energy (58) of the two electron spins:

$$\begin{aligned} U_S &= \tfrac{1}{2}\left(\rho_S^{++}-\rho_S^{--}\right)(\omega_{0S}+\omega'_{0S}) + \tfrac{1}{2}\left(\rho_J^{+}-\rho_J^{-}\right)\omega_J \\ &= -\tfrac{1}{4}\left(P_S+P'_S\right)(\omega_{0S}+\omega'_{0S}) + \tfrac{1}{2}\left(\rho_J^{+}-\rho_J^{-}\right)\omega_J \end{aligned} \tag{60}$$

where we insert (44). We rewrite this expression in such a way that we can subtract the Zeeman energy U_Z and U'_Z of the two electron spins and retain the electron interaction energy U_{SS}. To do so we recall the definition (13) of the angle θ, which enables us to write

$$\begin{aligned} \omega_{0S}+\omega'_{0S} &= 2\omega_{0S} - (\omega_{0S}-\omega'_{0S}) = 2\omega_{0S} - \omega_J\cos\theta, \\ \omega_{0S}+\omega'_{0S} &= 2\omega'_{0S} + (\omega_{0S}-\omega'_{0S}) = 2\omega'_{0S} + \omega_J\cos\theta. \end{aligned} \tag{61}$$

So, inserting (45),

$$\begin{aligned} &\tfrac{1}{4}\left(P_S+P'_S\right)(\omega_{0S}+\omega'_{0S}) \\ &\quad= \tfrac{1}{2}\omega_{0S}P_S + \tfrac{1}{2}\omega'_{0S}P'_S - \tfrac{1}{4}\left(P_S-P'_S\right)\omega_J\cos\theta \\ &\quad= -U_Z - U'_Z + \tfrac{1}{2}\left(\rho_J^{+}-\rho_J^{-}\right)\omega_J\cos^2\theta, \end{aligned} \tag{62}$$

Next we insert this expression in (60) and subtract U_Z and U'_Z. As a result we find

$$U_{SS} = \frac{1}{2}\left(\rho_J^{+}-\rho_J^{-}\right)\omega_J\sin^2\theta \tag{63}$$

for the electron interaction energy.

We now have all the elements needed to determine the flows of energy between the various reservoirs in the spin system. Combining (54) with the requirement of conservation of energy yields

$$\frac{\partial U_S}{\partial t} = -\frac{\partial U_I}{\partial t} = \frac{1}{2}\omega_{0I}\,\frac{\partial P_I}{\partial t}, \tag{64}$$

while combining (55) and (56) with (51) yields

$$\frac{\partial U_Z}{\partial t} = -\frac{1}{2}\omega_{0S}\,\frac{\partial P_S}{\partial t} = \frac{1}{2}\omega_{0S}\cos\theta\,\frac{\partial P_I}{\partial t} \tag{65}$$

and

$$\frac{\partial U'_Z}{\partial t} = -\frac{1}{2}\omega'_{0S}\,\frac{\partial P'_S}{\partial t} = -\frac{1}{2}\omega'_{0S}\cos\theta\,\frac{\partial P_I}{\partial t}. \tag{66}$$

So, inserting the matching condition $\omega_J = \omega_{0I}$,

$$\begin{aligned} \tfrac{\partial U_Z}{\partial t} + \tfrac{\partial U'_Z}{\partial t} &= \tfrac{1}{2}\left(\omega_{0S}-\omega'_{0S}\right)\cos\theta\,\tfrac{\partial P_I}{\partial t} \\ &= \omega_J\cos^2\theta\,\tfrac{\partial P_I}{\partial t} = \omega_{0I}\cos^2\theta\,\tfrac{\partial P_I}{\partial t} \\ &= -\cos^2\theta\,\tfrac{\partial U_I}{\partial t} \end{aligned} \tag{67}$$

Then, from (57) and (64) follows

$$\begin{aligned} \tfrac{\partial U_{SS}}{\partial t} &= \tfrac{\partial U_S}{\partial t} - \tfrac{\partial U_Z}{\partial t} - \tfrac{\partial U'_Z}{\partial t} \\ &= -\left(1-\cos^2\theta\right)\tfrac{\partial U_I}{\partial t} \\ &= -\sin^2\theta\,\tfrac{\partial U_I}{\partial t}. \end{aligned} \tag{68}$$

The resulting flows of energy are shown in Fig. 3. It shows a direct flow of energy proportional to $\sin^2\theta$ from the electron interaction reservoir to the nuclear spins and a flow of energy between the two electron Zeeman reservoirs, of which a part proportional to $\cos^2\theta$ is diverted to the nuclear spins. In an effort to render their definitions more precise, we denote the former flow of energy as *Thermal Mixing (TM)* and the latter flow as the *Cross Effect (CE)*. In the limit considered by the scrambled states approach the interaction between the two electron spins is assumed to be small compared to the nuclear Zeeman splitting. Then $D_{+-} \ll \omega_{0I}$, so $\cos^2\theta \approx 1$ and $\sin^2\theta \approx 0$, and the energy needed to flip the nuclear spin originates mainly in the electron Zeeman energy. In the limit considered by the fluctuating field approach polarization transfer to the nuclear spins is dominated by pairs of electron spins for which $D_{+-} \approx \omega_{0I}$, so $\cos^2\theta \approx 0$ and $\sin^2\theta \approx 1$. In that case the electron interaction reservoir is the main source of energy needed to flip the nuclear spin. The generalized treatment presented here considers the whole range of possible interactions between the electron spins. Then we see that triple spin flips induce the two energy flows simultaneously in single quantum mechanical transitions: a flow between the electron Zeeman reservoirs and the nuclear Zeeman reservoir proportional to $\sin^2\theta$ and a flow between the electron interaction reservoir and the nuclear Zeeman reservoir proportional to $\cos^2\theta$.

7. Spin temperature

While the previous section enabled us to interpret the left hand side of the rate Eq. (33) in terms of energy flows, we still need a physical interpretation of the right hand side. We obtain this using the concept of spin temperature. As a first step we rewrite this rate equation as follows

$$\begin{aligned} \tfrac{\partial P_I}{\partial t} &= -W_{SSI}\left(\rho_J^{+}\rho_I^{+} - \rho_J^{-}\rho_I^{-}\right) \\ &= -\tfrac{1}{2}W_{SSI}\left[\left(\rho_J^{+}+\rho_J^{-}\right)\left(\rho_I^{+}-\rho_I^{-}\right) - \left(\rho_J^{-}-\rho_J^{+}\right)\left(\rho_I^{+}+\rho_I^{-}\right)\right] \\ &= -\tfrac{1}{2}W_{SSI}\left[\left(\rho_J^{+}+\rho_J^{-}\right)P_I - \left(\rho_J^{-}-\rho_J^{+}\right)\right], \end{aligned} \tag{69}$$

where we insert (46) on the left hand side and the normalization (32) and our expression (34) for the polarization of the nuclear spin on the right hand side.

Next we introduce spin temperatures. Before doing so, a remark has to be made. In the description of the state of our three-spin system, spin temperatures need to be nothing more than parameters determining the diagonal components of the density matrix. Thus they do not need to be thermodynamic temperatures, and no thermal equilibrium is needed to introduce them. For our purposes it is sufficient to introduce them as follows: if $|n\rangle$ is an eigenstate of the unperturbed part $\mathcal{H}_0$ of the Hamiltonian and ω_n the corresponding energy level, then the spin temperatures T_n and their inverse $\beta_n = \hbar/k_B T_n$ are defined by

$$\langle n|\rho|n\rangle = \frac{1}{\Xi}\exp -\beta_n\omega_n, \tag{70}$$

Here $\hbar$ and k_B are Planck's and Boltzmann's constants, and

$$\Xi = \sum_n \exp -\beta_n\omega_n \tag{71}$$

is the sum of states, so $\mathrm{Tr}\{\rho\} = 1$.

Because the density matrix is factorized into a 2×2 matrix describing the state of the nuclear spin and a 4×4 matrix describing the state of the two electron spins, four spin temperatures are sufficient to define its diagonal elements. We describe the state of the nuclear spin with a spin temperature T_I and its inverse $\beta_I = \hbar/k_B T_I$, such that

$$\rho_I^{\pm} = \frac{1}{\Xi_I}\exp \pm\frac{1}{2}\omega_{0I}\beta_I, \tag{72}$$

in which

$$\Xi_I = \exp +\frac{1}{2}\omega_{0I}\beta_I + \exp -\frac{1}{2}\omega_{0I}\beta_I \tag{73}$$

is the sum of states for the nuclear spin. Then, upon insertion of these expressions in (34), we find that the nuclear spin polarization is given by the hyperbolic tangent

$$P_I = \tanh\frac{1}{2}\omega_{0I}\beta_I. \tag{74}$$

Notice that the inverse nuclear spin temperature β_I has the dimension of time, i.e. the inverse of frequency.

To describe the state of the two electron spins we follow Provotorov [11,12] and introduce three spin temperatures: the electron Zeeman temperatures T_Z and T'_Z and their inverse $\alpha = \hbar/k_B T_Z$ and $\alpha' = \hbar/k_B T'_Z$ and the electron interaction temperature T_{SS} and its inverse $\beta_{SS} = \hbar/k_B T_{SS}$ such that

$$\begin{aligned}
\rho_S^{++} &= \tfrac{1}{\Xi_S}\ \tilde{\rho}_S^{++} = \tfrac{1}{\Xi_S}\ \exp -\tfrac{1}{2}\left[\omega_{0S}\alpha + \omega'_{0S}\alpha'\right],\\
\rho_J^{+} &= \tfrac{1}{\Xi_S}\ \tilde{\rho}_J^{+} = \tfrac{1}{\Xi_S}\ \exp -\tfrac{1}{2}\left[\omega_{0S}\alpha - \omega'_{0S}\alpha' + (\omega_J - \omega_{0S} + \omega'_{0S})\beta_{SS}\right],\\
\rho_J^{-} &= \tfrac{1}{\Xi_S}\ \tilde{\rho}_J^{-} = \tfrac{1}{\Xi_S}\ \exp +\tfrac{1}{2}\left[\omega_{0S}\alpha - \omega'_{0S}\alpha' + (\omega_J - \omega_{0S} + \omega'_{0S})\beta_{SS}\right],\\
\rho_S^{--} &= \tfrac{1}{\Xi_S}\ \tilde{\rho}_S^{--} = \tfrac{1}{\Xi_S}\ \exp +\tfrac{1}{2}\left[\omega_{0S}\alpha + \omega'_{0S}\alpha'\right].
\end{aligned} \tag{75}$$

Here

$$\Xi_S = \tilde{\rho}_S^{++} + \tilde{\rho}_J^{+} + \tilde{\rho}_J^{-} + \tilde{\rho}_S^{--} \tag{76}$$

is the sum of states for the two electron spins. Thus the Boltzmann factors are split into two terms proportional to the Zeeman splitting of the two electron spins and one term proportional to their remaining energy.

We insert the definition (13) of the angle θ and execute the δ-function (25) in the transition rate W_{SSI}:

$$\begin{aligned}
\rho_S^{++} &= \tfrac{1}{\Xi_S}\ \exp -\tfrac{1}{2}\left[\omega_{0S}\alpha + \omega'_{0S}\alpha'\right],\\
\rho_J^{+} &= \tfrac{1}{\Xi_S}\ \exp -\tfrac{1}{2}\left[\omega_{0S}\alpha - \omega'_{0S}\alpha' + \omega_{0I}(1-\cos\theta)\beta_{SS}\right],\\
\rho_J^{-} &= \tfrac{1}{\Xi_S}\ \exp +\tfrac{1}{2}\left[\omega_{0S}\alpha - \omega'_{0S}\alpha' + \omega_{0I}(1-\cos\theta)\beta_{SS}\right],\\
\rho_S^{--} &= \tfrac{1}{\Xi_S}\ \exp +\tfrac{1}{2}\left[\omega_{0S}\alpha + \omega'_{0S}\alpha'\right].
\end{aligned} \tag{77}$$

The stationary state of our minimal system of two electron spins and one nuclear spin can now be characterized with a simple relation between the four inverse spin temperatures β_I, α, α' and β_{SS}. To derive it we notice that in such a state the left hand side of the rate Eq. (33) vanishes, and hence also the right hand side of (69). So

$$\left(\rho_J^- + \rho_J^+\right)P_I = \rho_J^- - \rho_J^+ \tag{78}$$

or

$$P_I = \frac{\rho_J^- - \rho_J^+}{\rho_J^- + \rho_J^+}. \tag{79}$$

We insert (74) for the nuclear spin polarization and (77) for the components of the density matrix. Then in the stationary state

$$\tanh\frac{1}{2}\omega_{0I}\beta_I = \tanh\frac{1}{2}\left[\omega_{0S}\alpha - \omega'_{0S}\alpha' + \omega_{0I}(1-\cos\theta)\beta_{SS}\right], \tag{80}$$

or

$$\omega_{0I}\beta_I = \omega_{0S}\alpha - \omega'_{0S}\alpha' + \omega_{0I}(1-\cos\theta)\beta_{SS}. \tag{81}$$

We discuss two limiting cases. First we consider pairs of electron spins for which $D_{+-} \ll \omega_{0I}$, so $\cos\theta \approx 1$. To investigate this limit, we set $\theta = 0$ in (77) and insert the result in (42) and (43). After some algebra we find that then the polarization of the two electron spins reduces to

$$P_S = \tanh\frac{1}{2}\omega_{0S}\alpha \quad \text{and} \quad P'_S = \tanh\frac{1}{2}\omega'_{0S}\alpha'. \tag{82}$$

and the diagonal components of the density matrix to

$$\begin{aligned}
\rho_S^{++} &= \tfrac{1}{4}(1-P_S)(1-P'_S),\\
\rho_J^{+} &= \tfrac{1}{4}(1-P_S)(1+P'_S),\\
\rho_J^{-} &= \tfrac{1}{4}(1+P_S)(1-P'_S),\\
\rho_S^{--} &= \tfrac{1}{4}(1+P_S)(1+P'_S).
\end{aligned} \tag{83}$$

We insert these expressions in the right hand side of the rate Eq. (69). As a result we find that the evolution of the nuclear spin polarization can be obtained from

$$\frac{\partial P_I}{\partial t} = -\frac{1}{4}W_{SSI}\left[(1-P_SP'_S)P_I - (P_S - P'_S)\right], \tag{84}$$

while, inserting $\cos\theta = 1$ in (51), the polarization of the two electron spins is found to evolve as

$$\frac{\partial P_S}{\partial t} = -\frac{1}{4}W_{SSI}\left[(1+P'_SP_I)P_S - (P'_S + P_I)\right], \tag{85}$$

$$\frac{\partial P'_S}{\partial t} = -\frac{1}{4}W_{SSI}\left[(1-P_SP_I)P'_S - (P_S - P_I)\right]. \tag{86}$$

These rate equations have the stationary solution

$$P_I = \frac{P_S - P'_S}{1 - P_SP'_S}, \tag{87}$$

which is precisely what would have been obtained by the scrambled states approach [18]—for a derivation using a similar notation see [10], Chapter 8. We write this result in terms of spin temperatures. We insert (82) for P_S and P'_S and apply the sum rule for hyperbolic tangents. Thus we find

$$\tanh\frac{1}{2}\omega_{0I}\beta_I = \tanh\frac{1}{2}\left[\omega_{0S}\alpha - \omega'_{0S}\alpha'\right]. \tag{88}$$

Notice that this expression is also directly obtained by setting $\cos\theta = 1$ in (80).

The other limiting case considers pairs of electron spins for which $D_{+-} \approx \omega_{0I}$, so $\cos\theta \approx 0$, while the matching condition corresponds to $\omega_{0S} \approx \omega'_{0S}$. Let us now suppose that the mutual interaction between the two electron spins then also renders $\alpha' \approx \alpha$. As a result

$$\rho_J^\pm \approx \frac{1}{\Xi_S} \exp \mp \frac{1}{2} \omega_{0I} \beta_{SS}. \tag{89}$$

So the rate Eq. (69) reduces to

$$\begin{aligned} \frac{\partial P_I}{\partial t} &= -\frac{1}{2} W_{SSI}\left(\rho_J^+ + \rho_J^-\right)\left[P_I - \frac{\rho_J^- - \rho_J^+}{\rho_J^+ + \rho_J^-}\right] \\ &= -\frac{1}{2} W_{SSI}\left(\rho_J^+ + \rho_J^-\right)\left[\tanh\frac{1}{2}\omega_{0I}\beta_I - \tanh\frac{1}{2}\omega_{0I}\beta_{SS}\right] \end{aligned} \tag{90}$$

and has a stationary solution

$$\beta_I \approx \beta_{SS}. \tag{91}$$

Notice that this result is also obtained by setting $\omega_{0S}\alpha_S = \omega'_{0S}\alpha'_S$ and $\cos\theta = 0$ in (81). Thus we find that the inverse nuclear spin temperature becomes equal to the inverse electron interaction temperature, precisely as is predicted by the fluctuating field approach in [14,15,13,16].

The two approaches converge to the same result if we assume that spectral diffusion across the ESR spectrum is fast and the electron spin system is in a local equilibrium, Provotorov's theory of cross relaxation [12] and its extension beyond the high temperature approximation [25,26] predict that

$$\omega_{0S}\alpha - \omega'_{0S}\alpha' = \left(\omega_{0S} - \omega'_{0S}\right)\beta_{SS}. \tag{92}$$

As a result one always finds (91) for the inverse nuclear spin temperature, just as follows from the fluctuation field approach. Notice that one can directly verify experimentally whether (91) holds: when DNP is performed on samples containing more than one nuclear spin species, the inverse nuclear spin temperature will tend to the same value β_{SS} for all nuclear spin species. Such observations have been reported from early on in DNP. See e.g. [30,31] and more recently [32,33].

It should be stressed however, that in the absence of fast spectral diffusion, (87) or (91) only hold in the limiting cases of a small or a strong mutual interaction respectively. In the intermediate range of mutual interactions one has to resort to the full condition (81).

8. Conclusions

This article presents a generalized approach for the treatment of triple spin flips involving two electron spins and one nuclear spin. It shows that they constitute a single process leading to two flows of energy: a flow of electron Zeeman energy to the nuclear spins and simultaneously a flow of electron interaction energy. The former is denoted as the cross effect (CE) and the latter as thermal mixing (TM). It is also found that the fluctuating field approach and the scrambled states approach are actually two distinct limiting cases of this more general approach. The scrambled states approach only considers transitions, in which two electron spins with Zeeman splittings $\omega_{0S} - \omega'_{0S} \approx \omega_{0I}$ flip together with a nuclear spin, so the energy needed to flip the nuclear spin originates in the Zeeman energy of the electron spins. The fluctuating field approach only considers transitions, in which two electron spins with Zeeman splittings $\omega_{0S} \approx \omega'_{0S}$ and a strong mutual interaction, such that $D_{+-} \approx \omega_{0I}$ flip together with a nuclear spin, so the energy needed to flip the nuclear spin originates in the mutual interaction between the electron spins.

This observation may not be limited to the triple spin flips considered here. It may e.g. also apply to direct nuclear spin-lattice relaxation, in which the spin-phonon interaction of electron spins combines with their hyperfine or super-hyperfine interaction with the nuclear spins to flip the latter. In the scrambled states approach, electron spins with Zeeman splitting ω_{0S} and phonon modes with energy ω_{ph}, such that $|\omega_{0S} - \omega_{ph}| \approx \omega_{0I}$ flip together with the nuclear spins, so the energy needed to flip the nuclear spins originates in the difference between the Zeeman energy of the electron spins and the energy of the phonon modes. In the fluctuating field approach $\omega_{0S} \approx \omega_{ph}$, and the energy needed to flip the nuclear spins originates in the spin-phonon interaction. However, in this case experimental verification of this distinction may not be easy, as the two approaches yield the same result [9].

In this paper we treat triple spin flips by first determining the exact eigenstates of the two interacting electron spins and next studying transitions involving these exact eigenstates and the nuclear spin states. As demonstrated in Appendix A this procedure is analogous to the procedure used in treatments of the solid effect in e.g. [34] and of pulsed DNP techniques like nuclear orientation via electron spin locking (NOVEL) [22] and the integrated solid effect (ISE) [23]. Then one first determines the exact eigenstates of electron spins interacting with a microwave field and next studies simultaneous transitions between these exact eigenstates and the nuclear spin states. In the latter two studies the polarization transfer is found to be coherent when both the microwave field and the hyperfine or super-hyperfine interaction are strong. One should therefore be aware that coherent effects can neither be excluded for triple spin flips when both the mutual interaction between the electron spins and the hyperfine or super-hyperfine interaction are strong.

The generalized approach presented here identifies two flows of energy from the two electron spins to the nuclear spin: a flow of Zeeman energy between the electron spins, of which part is diverted to the nuclear spin and a flow of interaction energy to the nuclear spin. In an effort to render their definitions more precise, the former is denoted as the cross effect (CE) and the latter as thermal mixing (TM). In the following article [24] this work is extended to a model system consisting of N_S randomly distributed and oriented electron spins and N_I equivalent nuclear spins.

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Appendix A. Analogy with the solid effect

In this Appendix we investigate the analogy between the treatment of triple spin flips in this article and the treatment of the solid effect in e.g. [34] and of pulsed DNP techniques like NOVEL and ISE [22,23]. For this purpose we consider a minimum system consisting of a single electron spin $S = \frac{1}{2}$ interacting with a single nuclear spin $I = \frac{1}{2}$ subjected to a static magnetic field and a microwave field $2B_1 \cos\omega t$ perpendicular to this static magnetic field. We describe this minimum system with the Hamiltonian

$$\mathcal{H} = \omega_{0S}S_z - \omega_{0I}I_z + 2\omega_{1S}S_x \cos\omega t + \frac{1}{2}S_z(A_{z-}I_+ + A_{z+}I_-). \tag{A.1}$$

Here the z-axis of the laboratory frame of reference is chosen along the static magnetic field and the x-axis along the microwave field, while $I_\pm = I_x \pm iI_y$. As in Section 2 Planck's constant $\hbar$ is skipped in the Hamiltonian, so the energy is expressed in frequency units. The first and the second term represent the Zeeman interaction of the electron and nuclear spin with the static magnetic field and the third term the interaction of the electron spin with the microwave field. Here $\omega_{1S} = \gamma_S B_1$ and γ_S is the gyromagnetic ratio of the electron spin. The last term represents the part of the hyperfine interaction between the electron and nuclear spin responsible for polarization transfer between these two spins. As also in Section 2 all other components of this interaction are skipped.

We transform the electron spin coordinates to a frame of reference rotating with the microwave frequency about the z-axis. Then [27]

$$\mathcal{H}_{\mathrm{rot}} = (\omega_{0S} - \omega)S_z + \omega_{1S}S_x - \omega_{0I}I_z + \frac{1}{2}S_z(A_{z-}I_+ + A_{z+}I_-). \qquad (A.2)$$

As shown in Fig. A.4, in this frame of reference the electron spin is subjected to an effective frequency vector $\boldsymbol{\omega}_{\mathrm{eff}}$ with components $\omega_{0S} - \omega$ and ω_{1S} along the z and x-axes. It has a length

$$\omega_{\mathrm{eff}} = \sqrt{\Delta^2 + \omega_{1S}^2} \qquad (A.3)$$

and is tilted about the y-axis through an angle θ defined by

$$\sin\theta = \frac{\omega_{1S}}{\sqrt{\Delta^2 + \omega_{1S}^2}}. \qquad (A.4)$$

Notice that this effective frequency vector transforms into the effective frequency vector shown in Fig. 1, if we replace the microwave frequency ω_{m} by the Zeeman splitting ω'_{0S} of a second electron spin S' and ω_{1S} by the component D_{+-} of the mutual interaction between S and S'.

As for triple spin flips, conservation of energy requires that polarization transfer to the nuclear spin only occurs when the matching condition

$$\omega_{\mathrm{eff}} = \omega_{0I} \qquad (A.5)$$

is satisfied. This condition is represented by the circle in Fig. A.4, which is the equivalent of the circle in Fig. 2.

As discussed in [34,22,23] only the component P_S^{eff} of the electron spin polarization along the effective frequency vector $\boldsymbol{\omega}_{\mathrm{eff}}$ can be transferred to the nuclear spin. The associated change of the total energy U_S of the electron spin can then be split in a change of its Zeeman energy in the externally applied magnetic field and a change of its energy in the microwave field:

$$\begin{aligned} \frac{\partial U_S}{\partial t} &= -\tfrac{1}{2}\omega_{\mathrm{eff}}\,\frac{\partial P_S^{\mathrm{eff}}}{\partial t} \\ &= -\tfrac{1}{2}(\omega_{0S} - \omega_{\mathrm{m}})\,\frac{\partial P_S^{\mathrm{eff}}\cos\theta}{\partial t} - \tfrac{1}{2}\omega_{1S}\,\frac{\partial P_S^{\mathrm{eff}}\sin\theta}{\partial t} \\ &= -\tfrac{1}{2}\omega_{\mathrm{eff}}\,\cos^2\theta\,\frac{\partial P_S^{\mathrm{eff}}}{\partial t} - \tfrac{1}{2}\omega_{\mathrm{eff}}\,\sin^2\theta\,\frac{\partial P_S^{\mathrm{eff}}}{\partial t}. \end{aligned} \qquad (A.6)$$

Hence a fraction $\cos^2\theta$ of the transferred energy originates in the interaction of the electron spin S with the externally applied static magnetic field and a fraction $\sin^2\theta$ originates in the interaction of S with the microwave field. This splitting of the transferred energy is analogous to the splitting of the energy transfer to the nuclear spins by triple spin flips. As discussed in Section 6, a fraction $\cos^2\theta$ of the transferred energy then also originates in the Zeeman energy of the electron spins, but in that case the remaining fraction $\sin^2\theta$ originates in the interaction of S with S'.

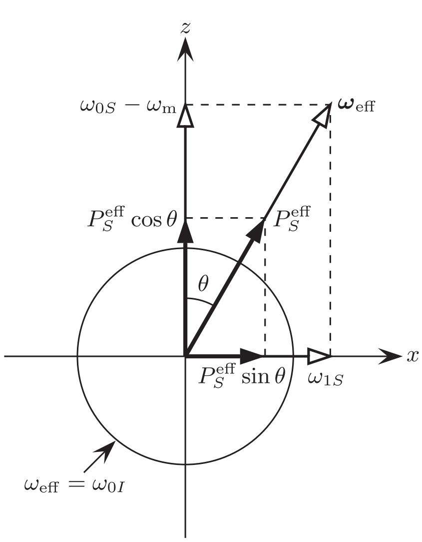

Fig. A.4. The effective frequency vector and the electron spin polarization in the rotating frame of reference. The circle represents the matching condition for polarization transfer in the solid effect.

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