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Dynamic nuclear polarization via the cross effect and thermal mixing: B. Energy transport

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ABSTRACT

The fundamental process of dynamic nuclear polarization (DNP) via the cross effect (CE) and thermal mixing (TM) is a triple spin flip, in which two interacting electron spins and a nuclear spin interacting with one of these electron spins flip together. In the previous article (Wenckebach, 2018) these triple spin flips were treated by first determining the eigenstates of the two interacting electron spins exactly and next investigating transitions involving these exact eigenstates and the nuclear spin states. It was found that two previously developed approaches—the scrambled states approach and the fluctuating field approach—are just two distinct limiting cases of this more general approach. It was also shown that triple spin flips constitute a single process causing two flows of energy: a flow originating in the electron Zeeman energy and a flow originating in the mutual interactions between the electron spins. In order to render their definitions more precise, the former flow was denoted as the CE and the latter as TM.

In this article the treatment is extended to a glass containing N_I equivalent nuclear spins $I = \frac{1}{2}$ and N_S randomly distributed and oriented electron spins $S = \frac{1}{2}$. Rate equations are derived for the two flows of energy to the nuclear spins. The flow originating in the electron Zeeman energy—i.e. the CE—is found to lead to the same stationary state as was previously predicted by the scrambled states approach, though the rate may be smaller due to limitations imposed by conservation of energy. The flow originating in the mutual interactions between the electron spins—i.e. TM—is found to involve the full spectrum of the mutual interactions between the electron spins, while the fluctuating field approach only accounts for the component of this spectrum at the nuclear magnetic resonance (NMR) frequency. Still, TM is found to induce equal spin temperature for different nuclear spin species during nuclear spin-lattice relaxation and, at least in some cases also during polarization.

It is also confirmed that TM couples local nuclear spins near the electron spins so strongly to the mutual interactions between electron spins, that they may constitute a single energy reservoir (Cox et al., 1973). Hence such local nuclear spins may have to be included in treatments of the dynamics of the electron spins.

1. Introduction

Dynamic nuclear polarization (DNP) is a powerful tool to study the role of spin in nuclear and particle physics, to enhance nuclear magnetic resonance (NMR) signals and to increase contrast in magnetic resonance imaging (MRI)—for reviews of applications see [3–7], for reviews of methods and mechanisms see [8–12]. In the previous article [1] we considered DNP to polarize nuclear spins in insulating solids—in particular glasses—doped with an agent providing unpaired electron spins. For DNP 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.

The previous article concentrated on the family of mechanisms—known as the cross effect (CE) and thermal mixing (TM)—in which the microwave field first reduces the polarization of some electron spins. This implies an increase of the Zeeman energy of these electron spins in the externally applied magnetic field and a change of the energy of their mutual interactions [13]. Next these mutual interactions induce spectral diffusion, a process in which the reduction of electron spin polarization is spread over the other electron spins, and that involves an exchange between electron Zeeman and electron interaction energy [14]. Subsequently, the mutual interaction between the electron spins combines with their

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hyperfine and super-hyperfine interaction with the nuclear spins to exchange electron Zeeman and electron interaction energy with nuclear Zeeman energy, thus polarizing the nuclear spins. The fundamental transition for these two flows of energy involves two electron spins and one nuclear spin, and will be denoted in this article as a triple spin flip.

The previous article [1] provided an analysis of these triple spin flips in a glass containing nuclear spins $I = \frac{1}{2}$, and doped with radicals providing electron spins $S = \frac{1}{2}$. For this analysis it considered a minimal sub-system consisting of two interacting electron spins and a single nuclear spin interacting with one of the electron spins. It introduced a generalized approach that first calculates the eigenstates of the two electron spins exactly, and subsequently investigates the transitions induced by the super-hyperfine interaction between the nuclear spin and one of the electron spins. It was shown that two previous approaches—the scrambled states approach introduced by Kessenikh [15] and further developed by Hwang and Hill [16] and more recently by Vega and co-workers [17], and the fluctuating field approach introduced by Buishvili [18], Provotorov and Kozhushner [19,20] and subsequently further developed by Goldman [21]—are just two distinct limiting cases of this generalized approach.

It was furthermore demonstrated how a triple spin flip—in a single quantum mechanical transition—invokes simultaneously the two different flows of energy to the nuclear spins mentioned above: a flow originating in the Zeeman interaction of the electron spins with the externally applied magnetic field and a flow originating in the mutual interactions between the electron spins. In an effort to render their definitions more precise, the former flow was denoted as the cross effect (CE) and the latter flow as thermal mixing (TM). This is similar to Provotorov's description of magnetic resonance saturation: each transition transforms part of the microwave energy into electron Zeeman energy and part into electron interaction energy [14].

The present paper extends this analysis to a model system consisting of a glass containing N_I equivalent nuclear spins and N_S randomly distributed and oriented electron spins. Rate equations are derived for the two flows of energy and embedded in a set of equations describing DNP. Criteria are developed for the relative strength of these two flows We finish with a discussion of some implications of this work for the interpretation of experimental results.

2. Model system for triple spin flips

As in the previous article [1] we treat 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. But while the previous article just considered a minimum sub-system consisting of two electron spins S^i and S^j and a single nuclear spin I^k interacting with S^i, we now extend the description to a model system consisting of N_S electron spins S^i and N_I equivalent nuclear spins I^k. We choose the z-axis of the laboratory frame of reference along the externally applied magnetic field and define this extended model with the Hamiltonian

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

$$\mathcal{H}_S = \sum_i^{N_S} \mathcal{Z}_S^i + \sum_i^{N_S} \sum_{j \neq i}^{N_S} \mathcal{H}_{SS}^{ij}, \tag{2}$$

$$\mathcal{Z}_I = \sum_k^{N_I} \mathcal{Z}_I^k, \tag{3}$$

$$\mathcal{V} = \sum_i^{N_S} \sum_k^{N_I} \mathcal{V}^{ik}. \tag{4}$$

Here

$$\mathcal{Z}_S^i = \omega_{0S}^i S_z^i \tag{5}$$

and

$$\mathcal{Z}_I^k = -\omega_{0I} I_z^k \tag{6}$$

are the Zeeman interactions of the electron and nuclear spins with this externally applied magnetic field. Note that Planck's constant $\hbar$ is skipped in the Hamiltonian, so the energy is expressed in frequency units. Notice furthermore that the Zeeman splittings ω_{0S}^i may be different for different electron spins because of anisotropy of the g-tensor. Next

$$\mathcal{H}_{SS}^{ij} = \frac{1}{2}\left[D_{zz}^{ij} S_z^i S_z^j + D_{+-}^{ij}\left(S_+^i S_-^j + S_-^i S_+^j\right)\right], \tag{7}$$

in which $S_\pm^i = S_x^i \pm i S_y^i$, represents the truncated mutual interaction between the electron spins [22]. For DNP the concentration of electron spins is generally low—typically $1 \cdot 10^{19}$ to $4 \cdot 10^{19}$ cm^{-3} (16–66 mM)—and the mutual interaction between electron spins is almost purely dipolar. Then $D_{zz} = 2D_{+-}$ and real.[1] In what follows we skip the terms $D_{zz}^{ij} S_z^i S_z^j$ as its expectation value does not change in triple spin flips involving S^i and S^j, nor do they induce transitions. Thus we ignore level shifts due to this term. In Section 10 the consequences of this simplification will be discussed in more detail, in particular in relation to the work of Karabanov et al. [23]. Finally

$$\mathcal{V}^{ik} = \frac{1}{2} S_z^i \left(A_{z-}^{ik} I_+^k + A_{z+}^{ik} I_-^k\right), \tag{8}$$

in which $I_\pm^k = I_x^k \pm i I_y^k$, represents the hyperfine and super-hyperfine interaction between the electron spins and the nuclear spins. Notice that all terms in the latter interaction are skipped except those inducing nuclear spin flips. Thus we also ignore shifts of the energy levels due to the interaction between the electron spins and the nuclear spins surrounding them. As already mentioned in the previous article [1], this is not a trivial simplification: in their treatment of Borghini's model [24] Abragam and Goldman pointed out that this can only be justified when the electron spin resonance (ESR) line is mainly broadened by g-tensor anisotropy [11]—which is fortunately mostly the case for paramagnetic centres in glasses. When—as in single crystals—the ESR line is mainly broadened by the hyperfine interaction with nearby nuclear spins, its shape changes when these nearby nuclear spins are polarized. As a result the rates of microwave saturation, of spectral diffusion and of triple spin flips change. This leads to a complex situation, as the polarization rate of the nearby nuclei depends in turn on these rates.

As in the previous article [1] our aim is to derive equations for the flows of energy in the spin system. Also as in that paper we use an extension of the alternative scrambled states approach introduced in [12], in which

$$\mathcal{H}_0 = \mathcal{H}_S + \mathcal{Z}_I \tag{9}$$

is considered as the unperturbed Hamiltonian and $\mathcal{V}$ as the perturbation. Then the flows of energy in the spin system follow from the evolution in time of the expectation value

$$U_n = \frac{\mathrm{Tr}\{\rho \mathcal{H}_n\}}{\mathrm{Tr}\{\rho\}} \tag{10}$$

of the various terms $\mathcal{H}_n$ in $\mathcal{H}_0$. Here ρ is the density matrix. To obtain this evolution we need to solve the Liouville equation. We exclude longitudinal relaxation and assume as initial condition that the density matrix is diagonal on a basis of eigenstates of $\mathcal{H}_0$. Then, as shown by Zwanzig [25], the Liouville equation can be reduced to

[1] See footnote in Appendix A.

a set of rate equations for the diagonal elements of ρ on a basis of eigenstates of $\mathcal{H}_0$, and in which the transition rates are given by Fermi's golden rule.

We consider the structure of the diagonal part ρ_0 of the density matrix in more detail. Because we ignore the mutual interaction between the nuclear spins and consider the hyperfine and super-hyperfine interaction to be first order, it can be factorized into a component ρ_S for the electron spins and N_I components ρ_k for the nuclear spins. Next we recall that for DNP the concentration of electron spins is generally low—typically $1\cdot10^{19}$–$4\cdot10^{19}$ cm^{-3} (16–66 mM)—and that we assume the electron spins to be randomly distributed and oriented. This incites us to describe them as a set of clusters of increasing size—single electron spins, pairs of electron spins, triples of electron spins, etc.—such that the interaction between electron spins belonging to different clusters is so weak, that we can approximate the density matrix by factorizing it in independent components, each corresponding to a cluster. Then the fraction of spins in pairs is proportional to the concentration of electron spins, the fraction of spins in triples proportional to the square of the concentration, etc. We now assume that the concentration of electron spins is sufficiently low, so we can ignore triples and larger clusters of electron spins. As a result we can approximate

$$\rho_S \approx \prod_{i,i+1}\rho_{i,i+1}\prod_{j\neq i,i+1}\rho_j, \tag{11}$$

in which all $\rho_{i,i+1}$ describe the state of the more strongly interacting pairs of electron spins and all ρ_j describe the state of all other electron spins.

3. Polarization transfer

We summarize some results from the previous paper [1]. In its description of triple spin flips, it considered a minimal subset of the model system described above. It consists of two interacting electron spins S^i and S^j and a single nuclear spin I^k interacting with S^i. The electron spin part

$$\mathcal{H}_S^{ij} = \mathcal{Z}_S^i + \mathcal{Z}_S^j + \mathcal{H}_{SS}^{ij} \tag{12}$$

of the Hamiltonian was first diagonalized. Next a rate equation was derived for the evolution of the polarization

$$P_I^k = \frac{1}{I}\frac{\mathrm{Tr}\{\rho_k I_z^k\}}{\mathrm{Tr}\{\rho_k\}} = \rho_k^+ - \rho_k^-. \tag{13}$$

of I^k, due to the term $\mathcal{V}^{ik}$ in the super-hyperfine interaction. Here

$$\rho_k = \begin{pmatrix}\rho_k^- & 0\\ 0 & \rho_k^+\end{pmatrix} \tag{14}$$

is the normalized density matrix describing the state of I^k on a basis of eigenstates of I_z^k, so

$$\mathrm{Tr}\{\rho_k\} = \rho_k^+ + \rho_k^- = 1. \tag{15}$$

The result was

$$\frac{\partial P_I^k}{\partial t} = -W_{\mathrm{SSI}}^{ijk}\left(\rho_{ij}^+\rho_k^+ - \rho_{ij}^-\rho_k^-\right), \tag{16}$$

in which

$$W_{SSI}^{ijk} = \frac{\pi}{2}\frac{|\frac{1}{2}A_{z+}^{ik}|^2\left(D_{+-}^{ij}\right)^2}{\omega_{0I}^2}\,\delta\left(\omega_{0I} - \sqrt{\left(\omega_{0S}^i - \omega_{0S}^j\right)^2 + \left(D_{+-}^{ij}\right)^2}\right) \tag{17}$$

is the transition rate, and

$$\rho_{ij} = \begin{pmatrix}\rho_{ij}^{++} & 0 & 0 & 0\\ 0 & \rho_{ij}^{+} & 0 & 0\\ 0 & 0 & \rho_{ij}^{-} & 0\\ 0 & 0 & 0 & \rho_{ij}^{--}\end{pmatrix} \tag{18}$$

is the normalized density matrix describing the state of the two electron spins on a basis of eigenstates of $\mathcal{H}_S^{ij}$, so

$$\mathrm{Tr}\{\rho_{ij}\} = \rho_{ij}^{++} + \rho_{ij}^{+} + \rho_{ij}^{-} + \rho_{ij}^{--} = 1. \tag{19}$$

The assumption that the density matrix can be factorized as in (11) enables us to extend the results for two electron spins S^i and S^j and one nuclear spin I^k to our model system consisting of N_S electron spins and N_I nuclear spins by simple addition over all these electron and nuclear spins. Then the evolution of the average nuclear spin polarization

$$P_I = \frac{1}{N_I}\sum_k^{N_I} P_I^k \tag{20}$$

due to triple spin flips is given by

$$\begin{aligned}\frac{\partial P_I}{\partial t} &= -\frac{1}{N_I}\sum_k^{N_I}\sum_i^{N_S}\sum_{j\neq i}^{N_S} W_{\mathrm{SSI}}^{ijk}\left(\rho_{ij}^+\rho_k^+ - \rho_{ij}^-\rho_k^-\right)\\ &= -\frac{\pi}{2}\frac{1}{N_I}\sum_k^{N_I}\sum_i^{N_S}\sum_{j\neq i}^{N_S}\frac{|\frac{1}{2}A_{z+}^{ik}|^2\left(D_{+-}^{ij}\right)^2}{\omega_{0I}^2}\\ &\quad\left(\rho_{ij}^+\rho_k^+ - \rho_{ij}^-\rho_k^-\right)\delta\left(\omega_{0I} - \sqrt{\left(\omega_{0S}^i - \omega_{0S}^j\right)^2 + \left(D_{+-}^{ij}\right)^2}\right).\end{aligned} \tag{21}$$

Here $\rho_{ij}^{\pm}$ can be factorized into $\rho_i^{\pm}\rho_j^{\mp}$ for pairs of more weakly interacting electron spins, but not for pairs of more strongly interacting electron spins.

Recall that we treat glasses, in which randomly distributed and oriented radicals provide the electron spins. As a consequence the components A_{z+}^{ik} of the hyperfine and super-hyperfine interaction between the electron and nuclear spins are neither correlated with the components D_{+-}^{ij} of the mutual interaction between the electron spins nor with their Zeeman splittings ω_{0S}^i. This enables us to replace the sum over $|\frac{1}{2}A_{z+}^{ik}|^2$ and the density matrix ρ_k by their averages

$$A^2 = \frac{1}{N_S}\sum_i^{N_S}\sum_k^{N_I}|\frac{1}{2}A_{z+}^{ik}|^2 \tag{22}$$

and

$$\rho_I = \begin{pmatrix}\rho_I^- & 0\\ 0 & \rho_I^+\end{pmatrix} = \frac{1}{N_I}\sum_k^{N_I}\rho_k = \frac{1}{N_I}\sum_k^{N_I}\begin{pmatrix}\rho_k^- & 0\\ 0 & \rho_k^+\end{pmatrix}. \tag{23}$$

Notice that the normalization (15) implies that also ρ_I is normalized:

$$\mathrm{Tr}\{\rho_I\} = \rho_I^+ + \rho_I^- = 1, \tag{24}$$

and that insertion of our expression (13) for the polarization of I^k into the average nuclear spin polarization (20) yields

$$P_I = \rho_I^+ - \rho_I^-. \tag{25}$$

Thus (21) simplifies to

$$\begin{aligned}\frac{\partial P_I}{\partial t} &= -\frac{\pi}{2}\frac{1}{N_I}\frac{A^2}{\omega_{0I}^2}\sum_i^{N_S}\sum_{j\neq i}^{N_S}\left(D_{+-}^{ij}\right)^2\left(\rho_{ij}^+\rho_I^+ - \rho_{ij}^-\rho_I^-\right)\\ &\quad\times\delta\left(\omega_{0I} - \sqrt{\left(\omega_{0S}^i - \omega_{0S}^j\right)^2 + \left(D_{+-}^{ij}\right)^2}\right).\end{aligned} \tag{26}$$

Because the radicals providing the electron spins are randomly oriented and distributed, also the components D^{ij}_{+-} of the mutual interactions between the electron spins are uncorrelated with their Zeeman splittings ω^i_{0S}. This enables us to average separately over the components D^{ij}_{+-} of these mutual interactions:

$$\frac{\partial P_I}{\partial t} = -\frac{\pi}{2}\frac{1}{N_I N_S^2}\frac{A^2}{\omega_{0I}^2}\sum_i^{N_S}\sum_{j\neq i}^{N_S}\sum_l^{N_S}\sum_{m\neq l}^{N_S}\left(D^{lm}_{+-}\right)^2\left(\rho^+_{ij}\rho^+_I - \rho^-_{ij}\rho^-_I\right) \times \delta\left(\omega_{0I} - \sqrt{\left(\omega^i_{0S}-\omega^j_{0S}\right)^2 + \left(D^{lm}_{+-}\right)^2}\right). \tag{27}$$

As a sidestep let us suppose that $D^{lm}_{+-} \ll \omega_{0I}$ for all pairs of electron spins in the sample. Then we may approximate this rate equation by skipping the term $\left(D^{lm}_{+-}\right)^2$ in the δ-function and insert

$$M_2 = \frac{1}{N_S}\sum_l^{N_S}\sum_{m\neq l}^{N_S}\left(D^{lm}_{+-}\right)^2, \tag{28}$$

so the rate equation simplifies to

$$\frac{\partial P_I}{\partial t} = -\frac{\pi}{2}\frac{1}{N_I N_S}\frac{A^2 M_2}{\omega_{0I}^2}\sum_i^{N_S}\sum_{j\neq i}^{N_S}\left(\rho^+_{ij}\rho^+_I - \rho^-_{ij}\rho^-_I\right)\delta\left(\omega_{0I} - |\omega^i_{0S} - \omega^j_{0S}|\right). \tag{29}$$

As a result our treatment reduces to the alternative scrambled states approach for triple spin flips as presented in [12], which ends up to be completely equivalent to the scrambled states approach as introduced by Kessenikh [15] and further developed by Hwang and Hill [16].

This approximation cannot always be justified, however. For electron spins with $g = 2, D^{ij}_{+-}/2\pi$ may reach values of up to 50 MHz if we assume their minimum distance to be 1 nm and their interaction to be purely dipolar. This estimate increases to 400 MHz, when the minimum distance is decreased to 0.5 nm. Thus, while for proton spins at 7 T—so $\omega_{0I}/2\pi = 298$ MHz—one can possibly defend such an approximation, for ^{13}C spins at 3.5 T—so $\omega_{0I}/2\pi = 37.5$ MHz—it cannot be justified so easily. Therefore, in what follows we continue with the general rate Eq. (27).

4. Distribution functions

We introduce distribution functions in order to replace the sums over the electron spins by integrals. We define the inhomogeneous electron spin resonance (ESR) lineshape $g_i(\omega)$ such that $g_i(\omega)d\omega$ is the probability that $\omega \leqslant \omega^i_{0S} < \omega + d\omega$. Similarly, $g_i(\omega-\Delta)d\omega$ is the probability that $\omega - \Delta \leqslant \omega^j_{0S} < \omega - \Delta + d\omega$. As a result we can replace sums over S^i and S^j by integrals over the inhomogeneous lineshape:

$$\frac{1}{N_S^2}\sum_i^{N_S}\sum_{j\neq i}^{N_S} f\left(\omega^i_{0S}, \omega^j_{0S}\right) = \int_{-\infty}^{\infty} d\Delta \int_{-\infty}^{\infty} d\omega\, g_i(\omega) g_i(\omega-\Delta) f(\omega, \omega-\Delta). \tag{30}$$

We furthermore introduce a distribution function $g_D(D)$ such that

$$\frac{1}{N_S}\sum_l^{N_S}\sum_{m\neq l}^{N_S} f\left(D^{lm}_{+-}\right) = \int_{-\infty}^{\infty} dD\, f(D) g_D(D). \tag{31}$$

An analytic expression for this distribution function is derived in Appendix A. It is found to be a Lorentzian

$$g_D(D) = \frac{D_D}{\pi\left(D^2 + D_D^2\right)} \tag{32}$$

with a width D_D and cut-off at a frequency D_0 corresponding to the maximum possible value of $|D^{lm}_{+-}|$. As noticed in Appendix A, this distribution function assumes the role of the spectrum of fluctuations in the fluctuating field approach. As also remarked in Appendix A, it cannot be interpreted such that $g_D(D)dD$ is the probability that $D \leqslant D^{lm}_{+-} < D + dD$. Rather $g_D(D)dD$ is the probability that the x and y-components of the local field experienced by the electron spins due their interaction with all other electron spins lie in the range between $\gamma_S^{-1}D$ and $\gamma_S^{-1}(D + dD)$, in which γ_S is the average gyromagnetic ratio of the electron spins.

Because the components D^{lm}_{+-} of the mutual interaction between the electron spins are not correlated with their resonance frequencies ω^i_{0S}, the distribution function $g_D(D)$ is not correlated with the inhomogeneous lineshape $g_i(\omega)$, and we can integrate over these two distribution functions separately. As a result, upon replacing the sums over S^i, S^j, S^l and S^m in (27) by integrals, the average nuclear spin polarization (20) is found to evolve as

$$\frac{\partial P_I}{\partial t} = \int_{-\infty}^{\infty} d\Delta \int_{-\infty}^{\infty} d\omega\, g_i(\omega) g_i(\omega-\Delta) \int_{-\infty}^{\infty} dD\, g_D(D) F(\omega, \Delta, D) \tag{33}$$

in which

$$F(\omega,\Delta,D) = -\frac{\pi}{2}\frac{N_S}{N_I}\frac{A^2D^2}{\omega_{0I}^2}\left[\rho^+_S(\omega,\Delta)\rho^+_I - \rho^-_S(\omega,\Delta)\rho^-_I\right] \times \delta\left(\omega_{0I} - \sqrt{\Delta^2 + D^2}\right) \tag{34}$$

is the contribution to the evolution of the nuclear spin polarization P_I of all pairs of electron spins for which $\omega \leqslant \omega^i_{0S} < \omega + d\omega$ and $\omega - \Delta \leqslant \omega^j_{0S} < \omega - \Delta + d\omega$ and for which the x and y-components of the local field due their interaction with all other electron spins lie in the range between $\gamma_S^{-1}D$ and $\gamma_S^{-1}(D + dD)$. In particular

$$\rho_S(\omega,\Delta) = \begin{pmatrix} \rho^{++}_S(\omega,\Delta) & 0 & 0 & 0 \\ 0 & \rho^+_S(\omega,\Delta) & 0 & 0 \\ 0 & 0 & \rho^-_S(\omega,\Delta) & 0 \\ 0 & 0 & 0 & \rho^{--}_S(\omega,\Delta) \end{pmatrix} \tag{35}$$

is the average of the density matrix (18) over all pairs of electron spins for which $\omega \leqslant \omega^i_{0S} < \omega + d\omega$ and $\omega - \Delta \leqslant \omega^j_{0S} < \omega - \Delta + d\omega$.

The δ-function in this rate equation represents conservation of energy: the energy $\pm\omega_{0I}$ needed to flip a nuclear spin requires a change $\mp\sqrt{\Delta^2 + D^2}$ of the energy of the electron spins. That is: triple spin flips need to obey the matching condition

$$\omega_{0I} = \sqrt{\Delta^2 + D^2}. \tag{36}$$

Fig. 1 presents a graphical representation of this matching condition. It plots the difference Δ between the Zeeman energy of pairs of electron spins as a function of D, i.e. of the local field experienced by the electron spins due their interaction with all other electron spins. In this figure the matching condition is satisfied everywhere on the circle with radius ω_{0I}.

To continue we first integrate over the distribution function $g_D(D)$, subsequently execute the δ-function and finish integrating over the inhomogeneous lineshapes $g_i(\omega)$ and $g_i(\omega-\Delta)$. This requires a transformation of the δ-function in (33). It is a function

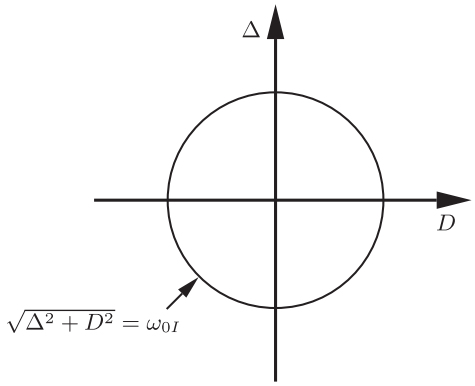

Fig. 1. Graphical representation of the matching condition $\omega_{0I} = \sqrt{\Delta^2 + D^2}$ required by the δ-function in the rate Eq. (33).

of the constant nuclear Zeeman splitting ω_{0I}, and to be able to execute it in the first integration, it needs to be a function of D. To transform it, we use the theorem[2] stating that

$$\delta(f(x)) = \sum_n \left|\frac{\partial f(x)}{\partial x}\right|^{-1}_{x=x_n} \delta(x - x_n) \tag{37}$$

if $f(x) = 0$ at $x = x_n$. We set

$$x = D, \tag{38}$$

then $f(x) = 0$ at

$$x_n = \pm\sqrt{\omega_{0I}^2 - \Delta^2}, \tag{39}$$

and

$$\left|\frac{\partial f(x)}{\partial x}\right|_{x=x_n} = \frac{|D|}{\omega_{0I}}. \tag{40}$$

As a result

$$\delta\left(\omega_{0I} - \sqrt{\Delta^2 + D^2}\right) = \frac{\omega_{0I}}{|D|}\,\delta\left(|D| - \sqrt{\omega_{0I}^2 - \Delta^2}\right). \tag{41}$$

Now we have written the δ-function as a function D, we can execute it in the integration over the distribution function $g_D(D)$ in (33). Then this rate equation reduces to

$$\frac{\partial P_I}{\partial t} = -\left[\int_{-\omega_{0I}}^{-\Delta_0} \mathrm{d}\Delta + \int_{\Delta_0}^{\omega_{0I}} \mathrm{d}\Delta\right] \int_{-\infty}^{\infty} \mathrm{d}\omega\, g_i(\omega) g_i(\omega - \Delta) \times \frac{N_S}{N_I}\, W_{SSI}(\Delta)\left[\rho_S^+(\omega,\Delta)\rho_I^+ - \rho_S^-(\omega,\Delta)\rho_I^-\right], \tag{42}$$

in which the integration limit $\Delta_0 = \sqrt{\omega_{0I}^2 - D_0^2}$ if $D_0 < \omega_{0I}$ and $\Delta_0 = 0$ otherwise. Notice also that the δ-function is obeyed twice, once for a positive value of D and once for a negative value. This is compensated in the integral over Δ by accounting for all values of $|\Delta|$ twice. Furthermore

$$W_{SSI}(\Delta) = \frac{\pi}{2} A^2 \frac{\sqrt{\omega_{0I}^2 - \Delta^2}}{\omega_{0I}} g_D\left(\sqrt{\omega_{0I}^2 - \Delta^2}\right) = \frac{\pi}{2} A^2 \frac{\sqrt{\omega_{0I}^2 - \Delta^2}}{\omega_{0I}} \frac{D_D}{\pi\left(\omega_{0I}^2 - \Delta^2 + D_D^2\right)}. \tag{43}$$

is the contribution to the transition rate of all pairs of electron spins for which $\Delta \leqslant \omega_{0S}^i - \omega_{0S}^j < \Delta + \mathrm{d}\Delta$.

We finish this section with another side step, in which we consider the limit $\Delta \to 0$, while assuming $\omega_{0I} \gg D_D$. Then

$$\lim_{\Delta\to 0} W_{SSI}(\Delta) \approx \frac{1}{2}\frac{A^2 D_D}{\omega_{0I}^2} \tag{44}$$

which is precisely the transition rate obtained by Goldman et al. using the fluctuating field approach [21].

5. Energy transfer

As in Section 3 we summarize some of the results of the previous article [1]. In that paper we determined the flows of energy in a minimal system of two electron spins S^i and S^j and one nuclear spin I^k. The total energy of these three spins was divided over four reservoirs. These were the nuclear spin reservoir containing the nuclear Zeeman energy

$$U_I^k = -\frac{1}{2}\omega_{0I} P_I^k, \tag{45}$$

two electron Zeeman reservoirs containing the Zeeman energy

$$U_Z^i = -\frac{1}{2}\omega_{0S}^i P_S^i \quad \text{and} \quad U_Z^j = -\frac{1}{2}\omega_{0S}^j P_S^j, \tag{46}$$

of the two electron spins and the electron interaction reservoir containing the energy U_{SS} of their mutual interaction. Here

$$P_S^i = -\frac{1}{S}\frac{\mathrm{Tr}\left\{\rho_{ij} S_z^i\right\}}{\mathrm{Tr}\left\{\rho_{ij}\right\}} \quad \text{and} \quad P_S^j = -\frac{1}{S}\frac{\mathrm{Tr}\left\{\rho_{ij} S_z^j\right\}}{\mathrm{Tr}\left\{\rho_{ij}\right\}} \tag{47}$$

are the polarization of the two electron spins, in which ρ_{ij} is given by (18). It was found that

$$\frac{\partial U_Z^i}{\partial t} + \frac{\partial U_Z^j}{\partial t} = -\left(\frac{\omega_{0S}^i - \omega_{0S}^j}{\omega_{0I}}\right)^2 \frac{\partial U_I^k}{\partial t} \tag{48}$$

$$\frac{\partial U_{SS}}{\partial t} = -\left[1 - \left(\frac{\omega_{0S}^i - \omega_{0S}^j}{\omega_{0I}}\right)^2\right] \frac{\partial U_I^k}{\partial t}. \tag{49}$$

So the energy needed to polarize the nuclear spin originates partly in the electron Zeeman energy and partly in the electron interaction energy. At this point we need to recall that we skipped the terms $D_{zz}^{ij} S_z^i S_z^j$ in the mutual interaction between the two electron spins. Thus we ignore their contribution to the energy U_{SS} of the mutual interactions between the electron spins. However, their expectation value is conserved in triple spin flips, so these terms do not contribute to the derivative (49) of U_{SS} with respect to time.

We extend this treatment to the N_S electron spins and N_I equivalent nuclear spins of the model system introduced in Section 2. From (42) follows immediately that the evolution in time of the total energy

$$U_I = -\frac{1}{2} N_I \omega_{0I} P_I \tag{50}$$

of the nuclear spins is the solution of

[2] Its proof is straightforward: if a continuous differentiable function $y(x)$ has zeros at $x = x_n$, then

$$\int_{-\infty}^{\infty} \mathrm{d}x\, \delta(y(x)) = \int_{-\infty}^{\infty} \mathrm{d}x \sum_n \delta\left(y(x_n) + \left(\frac{\partial y(x)}{\partial x}\right)_{x=x_n}(x - x_n)\right) = \int_{-\infty}^{\infty} \mathrm{d}x \sum_n \left|\frac{\partial y(x)}{\partial x}\right|^{-1}_{x=x_n} \delta(x - x_n),$$

where we use that $\delta(ax) = |a|^{-1}\delta(x)$.

$$\frac{\partial U_I}{\partial t} = \frac{1}{2}\omega_{0I} N_S \left[\int_{-\omega_{0I}}^{-\Delta_0} \mathrm{d}\Delta + \int_{\Delta_0}^{\omega_{0I}} \mathrm{d}\Delta\right] \int_{-\infty}^{\infty} \mathrm{d}\omega\, g_i(\omega) g_i(\omega-\Delta) \times W_{SSI}(\Delta)\left[\rho_S^+(\omega,\Delta)\rho_I^+ - \rho_S^-(\omega,\Delta)\rho_I^-\right], \tag{51}$$

where as in (42), the integration limit $\Delta_0 = \sqrt{\omega_{0I}^2 - D_0^2}$ if $D_0 < \omega_{0I}$ and $\Delta_0 = 0$ otherwise, while the transition rate $W_{SSI}(\Delta)$ is given by (43). We decompose this equation:

$$\frac{\partial U_I}{\partial t} = \left[\int_{-\omega_{0I}}^{-\Delta_0} \mathrm{d}\Delta + \int_{\Delta_0}^{\omega_{0I}} \mathrm{d}\Delta\right] \frac{\partial U_I(\Delta)}{\partial t}. \tag{52}$$

So

$$\frac{\partial U_I(\Delta)}{\partial t}\,\mathrm{d}\Delta, \tag{53}$$

in which

$$\frac{\partial U_I(\Delta)}{\partial t} = \frac{1}{2}\omega_{0I} N_S \int_{-\infty}^{\infty} \mathrm{d}\omega\, g_i(\omega) g_i(\omega-\Delta) \times W_{SSI}(\Delta)\left[\rho_S^+(\omega,\Delta)\rho_I^+ - \rho_S^-(\omega,\Delta)\rho_I^-\right], \tag{54}$$

is the contribution to the evolution of U_I by all pairs of electron spins S^i and S^j with Zeeman splittings $\Delta \leqslant \omega_{0S}^i - \omega_{0S}^j < \Delta + \mathrm{d}\Delta$.

The energy needed for this evolution originates in the total energy U_S of the electron spins. We split the flow of energy to the nuclear spins in a contribution from the total electron Zeeman energy

$$U_Z = \sum_i^{N_S} U_Z^i = \frac{1}{2}\sum_i^{N_S} \omega_{0S}^i P_S^i \tag{55}$$

of the electron spins and a contribution from the total electron interaction energy

$$U_{SS} = U_S - U_Z. \tag{56}$$

According to (48) we now expect the Zeeman energy of all pairs of electron spins S^i and S^j with Zeeman splittings $\Delta \leqslant \omega_{0S}^i - \omega_{0S}^j < \Delta + \mathrm{d}\Delta$ to evolve as

$$-\frac{\Delta^2}{\omega_{0I}^2}\frac{\partial U_I(\Delta)}{\partial t}, \tag{57}$$

while according to (49) we expect their interaction energy to evolve as

$$-\frac{\omega_{0I}^2 - \Delta^2}{\omega_{0I}^2}\frac{\partial U_I(\Delta)}{\partial t}. \tag{58}$$

Then, upon integration the total electron Zeeman energy is found to evolve as

$$\begin{aligned}\frac{\partial U_Z}{\partial t} &= -\left[\int_{-\omega_{0I}}^{-\Delta_0} \mathrm{d}\Delta + \int_{\Delta_0}^{\omega_{0I}} \mathrm{d}\Delta\right] \frac{\Delta^2}{\omega_{0I}^2}\frac{\partial U_I(\Delta)}{\partial t} \\ &= -\frac{1}{2}\omega_{0I} N_S \left[\int_{-\omega_{0I}}^{-\Delta_0} \mathrm{d}\Delta + \int_{\Delta_0}^{\omega_{0I}} \mathrm{d}\Delta\right] \int_{-\infty}^{\infty} \mathrm{d}\omega\, g_i(\omega) g_i(\omega-\Delta) \\ &\quad \times \frac{\Delta^2}{\omega_{0I}^2} W_{SSI}(\Delta)\left[\rho_S^+(\omega,\Delta)\rho_I^+ - \rho_S^-(\omega,\Delta)\rho_I^-\right],\end{aligned} \tag{59}$$

and the total electron interaction energy to evolve as

$$\begin{aligned}\frac{\partial U_{SS}}{\partial t} &= -\left[\int_{-\omega_{0I}}^{-\Delta_0} \mathrm{d}\Delta + \int_{\Delta_0}^{\omega_{0I}} \mathrm{d}\Delta\right] \frac{\omega_{0I}^2 - \Delta^2}{\omega_{0I}^2}\frac{\partial U_I(\Delta)}{\partial t} \\ &= -\frac{1}{2}\omega_{0I} N_S \left[\int_{-\omega_{0I}}^{-\Delta_0} \mathrm{d}\Delta + \int_{\Delta_0}^{\omega_{0I}} \mathrm{d}\Delta\right] \int_{-\infty}^{\infty} \mathrm{d}\omega\, g_i(\omega) g_i(\omega-\Delta) \\ &\quad \times \frac{\omega_{0I}^2 - \Delta^2}{\omega_{0I}^2} W_{SSI}(\Delta)\left[\rho_S^+(\omega,\Delta)\rho_I^+ - \rho_S^-(\omega,\Delta)\rho_I^-\right].\end{aligned} \tag{60}$$

Here, as in (42) and (51), the integration limit $\Delta_0 = \sqrt{\omega_{0I}^2 - D_0^2}$ if $D_0 < \omega_{0I}$ and $\Delta_0 = 0$ otherwise, while the transition rate $W_{SSI}(\Delta)$ is given by (43).

The three rate equations (51), (59) and (60) represent two distinct flows of energy to the nuclear spins: a flow of electron Zeeman energy and a flow of electron interaction energy. In the next section we will consider these two flows in more detail. As in the previous paper [1], in order to render their definition more precise, we will denote the former flow as the *Cross Effect (CE)* and the latter flow as *Thermal Mixing (TM)*.

6. The cross effect versus thermal mixing

Above we found that a single process—triple spin flips—induces two flows of energy: the CE exchange of electron Zeeman energy with nuclear spin energy and the TM exchange of electron interaction energy with nuclear spin energy. To compare these two flows of energy, Fig. 2 plots the factor

$$\frac{\Delta^2}{\omega_{0I}^2} W_{SSI}(\Delta) = \frac{\pi}{2} A^2 \frac{\Delta^2}{\omega_{0I}^2} \frac{\sqrt{\omega_{0I}^2 - \Delta^2}}{\omega_{0I}} \frac{D_D}{\pi\left(\omega_{0I}^2 - \Delta^2 + D_D^2\right)} \tag{61}$$

in the transition rate in (59) and the factor

$$\frac{\omega_{0I}^2 - \Delta^2}{\omega_{0I}^2} W_{SSI}(\Delta) = \frac{\pi}{2} A^2 \frac{\left(\omega_{0I}^2 - \Delta^2\right)^{3/2}}{\omega_{0I}^3} \frac{D_D}{\pi\left(\omega_{0I}^2 - \Delta^2 + D_D^2\right)}. \tag{62}$$

in the transition rate in (60) as a function of Δ. In this figure the drawn curve corresponds to the former—i.e. the CE flow of energy—and the dashed curve to the latter factor—i.e. the TM flow of energy. These curves were calculated choosing $D_D/\omega_{0I} = 10^{-2}$, which corresponds to e.g. ^{13}C spins at 5 T and electron spins with $g = 2$ at a concentration of $2.5 \cdot 10^{19}$ cm^{-3} (40 mM).

It is seen that the factor (61) is sharply peaked near $|\Delta| = \omega_{0I}$, so the CE exchange of electron Zeeman energy and nuclear Zeeman energy is strongly dominated by weakly interacting pairs of electron spins S^i and S^j, for which $|\omega_{0I}^i - \omega_{0I}^j| \approx \omega_{0I}$. On the other hand all pairs of electron spins contribute to the TM exchange of electron interaction energy and nuclear spin energy.

This allows for a significant simplification of the rate equation (59) for the CE flow of energy, but unfortunately not of the rate equation (60) for the TM flow. We investigate the simplification of the former. Because the CE flow of energy is dominated by pairs of electron spins for which $|\omega_{0I}^i - \omega_{0I}^j| \approx \omega_{0I}$ we can approximate the inhomogeneous line shape $g_i(\omega - \Delta)$ by $g_i(\omega - \omega_{0I})$ in the rate equation (59). We also replace the components $\rho_S^{\pm}(\omega,\Delta)$ of the density matrix describing the state of the electron spins by $\rho_S^{\pm}(\omega,\omega_{0I})$. Then, after furthermore inserting (43) for the transition rate $W_{SSI}(\Delta)$ and noticing that $\Delta^2/\omega_{0I}^2\, W_{SSI}(\Delta)$ is a symmetric function of Δ, this rate equation reduces to

$$\begin{aligned}\frac{\partial U_Z}{\partial t} &\approx -\omega_{0I} N_S \int_{\Delta_0}^{\omega_{0I}} \mathrm{d}\Delta \int_{-\infty}^{\infty} \mathrm{d}\omega\, g_i(\omega) g_i(\omega-\omega_{0I}) \\ &\quad \times \frac{\Delta^2}{\omega_{0I}^2} W_{SSI}(\Delta)\left[\rho_S^+(\omega,\omega_{0I})\rho_I^+ - \rho_S^-(\omega,\omega_{0I})\rho_I^-\right] \\ &= -\frac{1}{2}\omega_{0I} N_S W_{SSI}^Z \int_{-\infty}^{\infty} \mathrm{d}\omega\, g_i(\omega) g_i(\omega-\omega_{0I}) \\ &\quad \times \left[\rho_S^+(\omega,\omega_{0I})\rho_I^+ - \rho_S^-(\omega,\omega_{0I})\rho_I^-\right],\end{aligned} \tag{63}$$

in which

$$W_{SSI}^Z = \pi A^2 \int_{\Delta_0}^{\omega_{0I}} \mathrm{d}\Delta\, \frac{\Delta^2}{\omega_{0I}^2} \frac{\sqrt{\omega_{0I}^2 - \Delta^2}}{\omega_{0I}} \frac{D_D}{\pi\left(\omega_{0I}^2 - \Delta^2 + D_D^2\right)}. \tag{64}$$

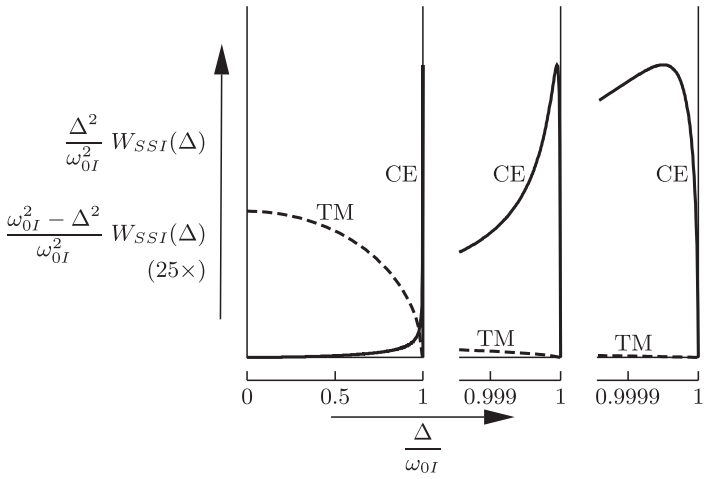

Fig. 2. The drawn and dashed curves represent the factors (61) and (62) respectively as a function of Δ/ω_{0I}. The vertical scale is in arbitrary units.

Thus, after inserting (50) we obtain the following rate equation for the evolution of the nuclear spin polarization due to the flow of electron Zeeman energy to the nuclear spins:

$$\left(\frac{\partial P_I}{\partial t}\right)_Z = -\frac{N_S}{N_I} W_{SSI}^Z \int_{-\infty}^{\infty} d\omega\, g_i(\omega) g_i(\omega - \omega_{0I}) \times \left[\rho_S^+(\omega, \omega_{0I})\rho_I^+ - \rho_S^-(\omega, \omega_{0I})\rho_I^-\right]. \tag{65}$$

As was observed above, all pairs of electron spins may contribute to the TM flow of electron interaction energy to or from the nuclear spins. As a result we cannot simplify the rate equation (60) for the transfer of electron interaction energy as easily as we simplified the rate equation (59) for the transfer of the electron Zeeman energy.

To get still an estimate of the TM transfer of electron interaction energy in comparison with the CE transfer of Zeeman energy, we compare the integral

$$W_{SSI}^{SS} = \left[\int_{-\omega_{0I}}^{-\Delta_0} d\Delta + \int_{\Delta_0}^{\omega_{0I}} d\Delta\right] \frac{\omega_{0I}^2 - \Delta^2}{\omega_{0I}^2} W_{SSI}(\Delta) = \pi A^2 \int_{\Delta_0}^{\omega_{0I}} d\Delta \frac{\left(\omega_{0I}^2 - \Delta^2\right)^{3/2}}{\omega_{0I}^3} \frac{D_D}{\pi\left(\omega_{0I}^2 - \Delta^2 + D_D^2\right)} \tag{66}$$

with the integral W_{SSI}^Z given by (64). As before, the integration limit $\Delta_0 = \sqrt{\omega_{0I}^2 - D_0^2}$ if $D_0 < \omega_{0I}$ and $\Delta_0 = 0$ otherwise.

Fig. 3 plots numerical results for W_{SSI}^Z and this integral as a function of the ratio D_0/ω_{0I} of the cut-off frequency D_0 and the nuclear Zeeman splitting ω_{0I}. We see that D_0 is the main parameter determining the relative rates at which the CE and TM transfer electron Zeeman and electron interaction energy to or from the nuclear spins. When D_0 is much smaller than ω_{0I}, the rate for TM is much smaller than for the CE. But it increases rapidly for larger values of D_0, and for $D_0 \geqslant \omega_{0I}$ both rates are equal.

A few approximations allow for an analytical comparison of the two flows of energy. We start noticing that in typical conditions for DNP the nuclear Zeeman splitting ω_{0I} is much larger than the width D_D of the distribution function $g_D(D)$. This incites us to skip the term D_D^2 in the denominator.[3] Then

$$W_{SSI}^Z \approx \frac{A^2 D_D}{\omega_{0I}^2} \int_0^{\omega_{0I}} d\Delta \frac{\Delta^2}{\omega_{0I}^2} \frac{\omega_{0I}}{\sqrt{\omega_{0I}^2 - \Delta^2}} = \frac{\pi}{4} \frac{A^2 D_D}{\omega_{0I}}, \tag{67}$$

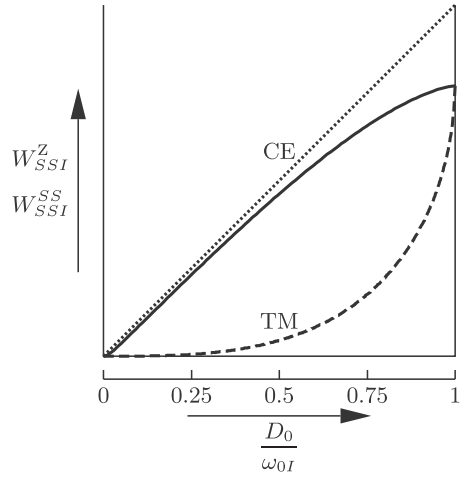

Fig. 3. The drawn and the dashed curve represent the transition rates W_{SSI}^Z and W_{SSI}^{SS} as a function of D_0/ω_{0I} respectively. The drawn curve is calculated using the exact expression (64) for W_{SSI}^Z and the dotted line corresponds to the approximation (70). The vertical scale is in arbitrary units.

when $D_0 \geqslant \omega_{0I}$, so $\Delta_0 = 0$, and[4]

$$W_{SSI}^Z \approx \frac{A^2 D_D}{\omega_{0I}^2} \int_{\sqrt{\omega_{0I}^2 - D_0^2}}^{\omega_{0I}} d\Delta \frac{\Delta^2}{\omega_{0I}^2} \frac{\omega_{0I}}{\sqrt{\omega_{0I}^2 - \Delta^2}}. = \frac{1}{2} \frac{A^2 D_D}{\omega_{0I}} \left[\frac{\pi}{2} - \arccos\frac{D_0}{\omega_{0I}} + \frac{D_0}{\omega_{0I}} \sqrt{1 - \frac{D_0^2}{\omega_{0I}^2}}\right]. \tag{68}$$

otherwise, so $\Delta_0 = \sqrt{\omega_{0I}^2 - D_0^2}$. The latter rather complicated expression can be simplified significantly when the cut-off frequency D_0 of the distribution function $g_D(D)$ is much smaller than ω_{0I}. Then we can expand

$$\arccos\frac{D_0}{\omega_{0I}} \approx \frac{\pi}{2} - \frac{D_0}{\omega_{0I}} - \frac{1}{3}\frac{D_0^3}{\omega_{0I}^3} + \cdots, \tag{69}$$

and up to lowest order we find

$$W_{SSI}^Z \approx \frac{A^2 D_D D_0}{\omega_{0I}^2} = \frac{\pi}{2} \frac{A^2 M_2}{\omega_{0I}^2}, \tag{70}$$

[3] It can be checked that the relative error in the result is of the order D_D/ω_{0I}.

[4] These integrals are most easily evaluated writing $\cos\theta = \Delta/\omega_{0I}$ and integrating over θ.

where we also insert the second moment (A.8). This expression is exactly what we would have obtained using the scrambled states approach—for a comparison using the same notation see [12], Chapter 8. Thus the scrambled states approach yields this rate for the transfer of energy in the limit that the cut-off frequency $D_0 \ll \omega_{0I}$.

Fig. 3 also plots the approximate expression (70)as a dotted line. As for the drawn curve in Fig. 2 we choose $D_D/\omega_{0I} = 10^{-2}$. It is seen that for $D_0/\omega_{0I} > 0.5$ the rate of energy transfer becomes smaller than determined by (70) and eventually, when $D_0 \geqslant \omega_{0I}$ it is limited to the value (67). This reduction and subsequent limitation have a simple origin: conservation of energy inhibits pairs of electron spins, for which $D^{ij}_{+-} > \omega_{0I}$, to participate in triple spin flips.

We continue with the integral W^{SS}_{SSI}. Again we skip the small term D_D^2 in the denominator.[5] Then for $D_0 \geqslant \omega_{0I}$, so $\Delta_0 = 0$, the integral W^{SS}_{SSI} simplifies to

$$W^{SS}_{SSI} \approx \frac{A^2 D_D}{\omega_{0I}^2} \int_0^{\omega_{0I}} \mathrm{d}\Delta \, \frac{\sqrt{\omega_{0I}^2 - \Delta^2}}{\omega_{0I}} = \frac{\pi}{4} \frac{A^2 D_D}{\omega_{0I}}, \tag{71}$$

while for $D_0 < \omega_{0I}$ it becomes[6]

$$W^{SS}_{SSI} \approx \frac{A^2 D_D}{\omega_{0I}^2} \int_{\sqrt{\omega_{0I}^2 - D_0^2}}^{\omega_{0I}} \mathrm{d}\Delta \, \frac{\sqrt{\omega_{0I}^2 - \Delta^2}}{\omega_{0I}}$$
$$= \frac{A^2 D_D}{2\omega_{0I}} \left[\frac{\pi}{2} - \arccos\frac{D_0}{\omega_{0I}} - \frac{D_0}{\omega_{0I}} \sqrt{1 - \frac{D_0^2}{\omega_{0I}^2}} \right]. \tag{72}$$

As for W^{Z}_{SSI}, this rather complicated expression can be simplified, when $D_0 \ll \omega_{0I}$, so we can insert the expansion (69). Then

$$W^{SS}_{SSI} \approx \frac{5}{12} \frac{A^2 D_D D_0^3}{\omega_{0I}^4}. \tag{73}$$

Upon comparison with (67) and (70) we see that $W^{Z}_{SSI} = W^{SS}_{SSI}$ when the cut-off frequency D_0 is larger than the NMR frequency ω_{0I}. Hence, for such larger values of D_0, transfer of electron Zeeman energy to the nuclear spins may be just as fast as transfer of electron interaction energy. However, if D_0 is smaller than ω_{0I}, TM transfer of electron interaction energy becomes slower than CE transfer of electron Zeeman energy by a factor

$$\frac{5}{12} \frac{D_0^2}{\omega_{0I}^2}, \tag{74}$$

so transfer of the latter type of energy rapidly dominates. Notice that the integral W^{SS}_{SSI} does not lead to the transition rate (44) found by the fluctuating field approach [21]. The reason is that in our calculation the whole spectrum $g_D(D)$ contributes to TM and not just the component for which $D \approx \omega_{0I}$.

It should be stressed that this comparison between transfer of electron Zeeman energy and transfer of electron interaction energy to the nuclear spins can only be tentative, as we cannot simplify the rate equation (60) for the evolution of the electron interaction energy in a similar way as the rate equation (59) for the evolution of the electron Zeeman energy.

7. Energy reservoirs

For a complete description of DNP via triple spin flips we need to add the microwave field, spectral diffusion transferring electron spin polarization across the ESR spectrum, electron spin-lattice relaxation and nuclear spin diffusion transferring nuclear spin polarization spatially. In this section we discuss a few possible scenarios depending on the relative rates of the CE and TM, and on how nuclear spin diffusion intervenes.

First we consider the case that the cut-off frequency D_0 of the distribution function $g_D(D)$ is much smaller than the Zeeman splitting ω_{0I} of the nuclear spins. Then transfer of electron interaction energy to the nuclear spins via TM is negligible compared to the transfer of electron Zeeman energy to these spins via the CE. This situation is depicted schematically in Fig. 4. The energy of the nuclear spins and the electron interaction energy are contained in two completely separated energy reservoirs: the nuclear spin reservoir and the electron interaction reservoir. Because only the CE transfers energy to the nuclear spins, existing theories of the CE can be used to describe DNP.

When the cut-off frequency D_0 is of the same order of magnitude as the Zeeman splitting ω_{0I} of the nuclear spins, we need to take transfer of electron interaction energy to the latter spins into account. This can be a fast process as the following estimate shows. Let us suppose that $D_0 > \omega_{0I}$, so the integral W^{SS}_{SSI} is given by (71). The integral

$$\int_{-\infty}^{\infty} \mathrm{d}\omega \, g_\mathrm{i}(\omega) g_\mathrm{i}(\omega - \Delta) \tag{75}$$

in the rate equation (60) is of the order of the inverse of the inhomogeneous line width Δ_i. Hence electron interaction energy is transferred to the nuclear spins at a total rate of the order

$$W_\mathrm{tot} = \frac{\pi}{4} \frac{A^2 D_D}{\omega_{0I} \Delta_\mathrm{i}}. \tag{76}$$

To estimate A^2 we need to take nuclear spin diffusion into account. Nuclear spin diffusion transfers nuclear Zeeman energy spatially across the sample and hence between nuclear spins near the electron spins and nuclear spins further away. The usual way to implement nuclear spin diffusion is to define a distance between the electron spins and the nuclear spins—the diffusion barrier—separating local nuclear spins near the electron spins from bulk nuclear spins further away [22]. Hyperfine interaction shifts the NMR frequency of the local nuclear spins to such an extend, that flip-flop transitions transferring polarization from these local nuclear spins to the bulk nuclear spins is inhibited. So we need to separate the TM and CE energy flows to the local nuclear spins from such flows to the bulk nuclear spins. Thus we obtain four energy flows as shown in Fig. 5. To calculate the rates of the energy transfer to the local nuclear spins, we need to sum over the local nuclear spins in our expression (22) for A^2. To calculate the rates of energy transfer to the bulk nuclear spins, we only include the bulk nuclear spins in this sum.

As an example we consider DNP of proton spins at a concentration of $0.75 \cdot 10^{23}$ cm^{-3} in samples doped with TEMPO with $g \approx 2$ at a concentration of $2 \cdot 10^{19}$ cm^{-3} (33 mM) and cooled to 1.2 K in a static magnetic fields of 3.4 T. Then $D_D/2\pi = 0.2$ MHz, $\omega_{0I}/2\pi = 145$ MHz and $\Delta_\mathrm{i}/2\pi = 100$ MHz. local proton spins can be as near as 2 Å from the electron spins. Then A^2 may be as large as $0.2 \cdot 10^{16}$ s^{-2}, and we find $W_\mathrm{tot} = 0.7 \cdot 10^4$ s^{-1}. This is much faster than the rate of electron spin-lattice relaxation, which was found in [26] to be $T_{1S}^{-1} = 2 \cdot 10^2$ s^{-1}. Hence—as was pointed out already by Cox et al. [2]—the Zeeman energy of the local nuclear spins and the electron interaction energy are contained in a single energy reservoir. Notice that this may have a profound effect on the dynamics of the electron spins.

How much of the energy of the bulk nuclear spins is also contained in this single reservoir, depends on the rate of the TM flow to the bulk nuclear spins compared to the rate of spin-lattice relax-

[5] In this case it can be checked that the relative error in the result is of the order D_D^2/ω_{0I}^2.

[6] As before these integrals are most easily evaluated writing $\cos\theta = \Delta/\omega_{0I}$ and integrating over θ.

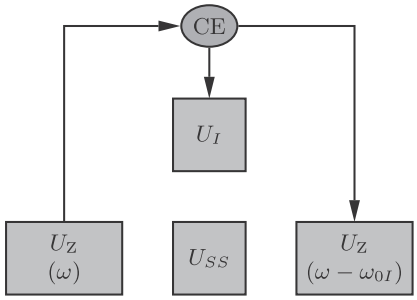

Fig. 4. Energy flows when the cut-off frequency D_0 is much smaller than the Zeeman splitting ω_{0I} of the nuclear spins, so only electron Zeeman energy is transferred to the nuclear spins via the CE.

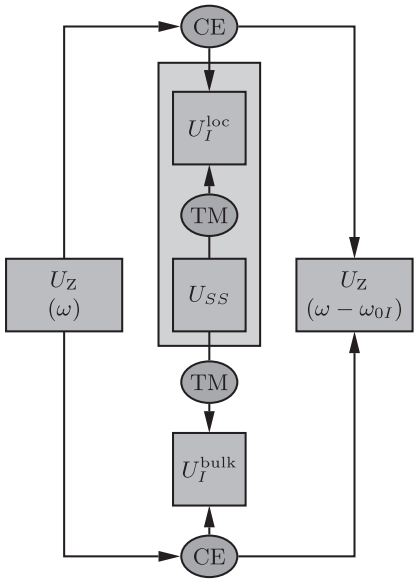

Fig. 5. Energy flows when the local nuclear spins are tightly coupled to the electron interaction reservoir via TM, but the bulk nuclear spins are more loosely coupled via TM.

ation of the electron interaction energy on the one hand and the rate of nuclear spin diffusion between the bulk nuclear spins on the other hand. Estimating the size of that combined energy reservoir is therefore not trivial, among further reasons because nuclear spin diffusion is not spherical, see e.g. [12], Chapter 6, and will not be attempted for our example.

8. Spin temperature and the stationary state

We continue with an investigation of the stationary state to which triple spin flips tend to lead. According to the rate equation (65), the CE branch of the energy flow tends to a stationary state obeying

$$\int_{-\infty}^{\infty} \mathrm{d}\omega\, g_{\rm i}(\omega) g_{\rm i}(\omega-\omega_{0I}) \left[\rho_S^+(\omega,\omega_{0I})\rho_I^+ - \rho_S^-(\omega,\omega_{0I})\rho_I^-\right] = 0. \tag{77}$$

For the TM branch we insert the rate (43) in the rate equation (60), while skipping the small term D_D^2 in the denominator. Thus we find that this branch leads to a stationary state obeying

$$\left[\int_{-\omega_{0I}}^{-\Delta_0} \mathrm{d}\Delta + \int_{\Delta_0}^{\omega_{0I}} \mathrm{d}\Delta\right] \int_{-\infty}^{\infty} \mathrm{d}\omega\, g_{\rm i}(\omega) g_{\rm i}(\omega-\Delta) \times \sqrt{\omega_{0I}^2 - \Delta^2}\, \left[\rho_S^+(\omega,\Delta)\rho_I^+ - \rho_S^-(\omega,\Delta)\rho_I^-\right] = 0. \tag{78}$$

in which, as usual, the integration limit $\Delta_0 = \sqrt{\omega_{0I}^2 - D_0^2}$ if $D_0 < \omega_{0I}$ and $\Delta_0 = 0$ otherwise.

We rewrite these equations as relations between spin temperatures. As in [1] we describe the state of the nuclear spins with a spin temperature T_I and its inverse $\beta_I = \hbar/k_{\rm B}T_I$, such that

$$\rho_I^{\pm} = \frac{1}{\Xi_I} \exp \pm \frac{1}{2}\omega_{0I}\beta_I. \tag{79}$$

Here $\hbar$ and $k_{\rm B}$ are Planck's and Boltzmann's constant, and

$$\Xi_I = \exp + \frac{1}{2}\omega_{0I}\beta_I + \exp - \frac{1}{2}\omega_{0I}\beta_I \tag{80}$$

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

As in [1] we follow Provotorov [13,14] to describe the state of the electron spins. Recall that in [1] we considered two interacting electron spins S^i and S^j with Zeeman splittings ω_{0S}^i and ω_{0S}^j and a nuclear spin I^k with a Zeeman splitting ω_{0I} interacting with S^i. To describe their state we introduced the electron Zeeman temperatures $T_{\rm Z}^i$ and $T_{\rm Z}^j$ and their inverse $\alpha^i = \hbar/k_{\rm B}T_{\rm Z}^i$ and $\alpha^i = \hbar/k_{\rm B}T_{\rm Z}^j$ and the electron interaction temperature T_{SS} and its inverse $\beta_{SS} = \hbar/k_{\rm B}T_{SS}$, such that the density matrix has diagonal elements

$$\begin{aligned} \rho_S^{\pm\pm} &= \tfrac{1}{\Xi_S}\, \widetilde{\rho}_S^{\pm\pm} \\ \rho_J^{\pm} &= \tfrac{1}{\Xi_S}\, \widetilde{\rho}_J^{\pm} \end{aligned} \tag{81}$$

in which

$$\begin{aligned} \widetilde{\rho}_S^{\pm\pm} &= \exp \mp \tfrac{1}{2}\left[\omega_{0S}^i\alpha^i + \omega_{0S}^j\alpha^j\right], \\ \widetilde{\rho}_J^{\pm} &= \exp \mp \tfrac{1}{2}\left[\omega_{0S}^i\alpha^i - \omega_{0S}^j\alpha^j + \left(\omega_{0I} - \omega_{0S}^i + \omega_{0S}^j\right)\beta_{SS}\right], \end{aligned} \tag{82}$$

and

$$\Xi_S = \widetilde{\rho}_S^{++} + \widetilde{\rho}_J^{+} + \widetilde{\rho}_J^{-} + \widetilde{\rho}_S^{--} \tag{83}$$

is the sum of states for the two electron spins.[7] Here we already executed the δ-function in the transition rate (17).

We extend this density matrix to our system consisting of N_I equivalent nuclear spins and N_S randomly distributed and oriented electron spins. To describe the state of all pairs of electron spins S^i and S^j, for which $\omega \leqslant \omega_{0S}^i < \omega + \mathrm{d}\omega$ and $\Delta \leqslant \omega_{0S}^i - \omega_{0S}^j < \Delta + \mathrm{d}\Delta$, we replace the inverse electron Zeeman temperatures α^i and α^j by their averages $\alpha(\omega)$ and $\alpha(\omega-\Delta)$ in these intervals. As Provotorov [13,14] we retain a single electron interaction temperature T_{SS} and its inverse $\beta_{SS} = \hbar/k_{\rm B}T_{SS}$. Thus we describe these pairs of electron spins with a density matrix with diagonal elements

$$\begin{aligned} \rho_S^{\pm\pm}(\omega,\Delta) &= \tfrac{1}{\Xi_S(\omega,\Delta)}\, \widetilde{\rho}_S^{\pm\pm}(\omega,\Delta) \\ \rho_S^{\pm}(\omega,\Delta) &= \tfrac{1}{\Xi_S(\omega,\Delta)}\, \widetilde{\rho}_S^{\pm}(\omega,\Delta) \end{aligned} \tag{84}$$

in which

$$\begin{aligned} \widetilde{\rho}_S^{\pm\pm}(\omega,\Delta) &= \exp \mp \tfrac{1}{2}[\omega\alpha(\omega) + (\omega-\Delta)\alpha(\omega-\Delta)], \\ \widetilde{\rho}_S^{\pm}(\omega,\Delta) &= \exp \mp \tfrac{1}{2}[\omega\alpha(\omega) - (\omega-\Delta)\alpha(\omega-\Delta) + (\omega_{0I}-\Delta)\beta_{SS}] \end{aligned} \tag{85}$$

and

$$\Xi_S(\omega,\Delta) = \widetilde{\rho}_S^{++}(\omega,\Delta) + \widetilde{\rho}_S^{+}(\omega,\Delta) + \widetilde{\rho}_S^{-}(\omega,\Delta) + \widetilde{\rho}_S^{--}(\omega,\Delta) \tag{86}$$

is the sum of states for these pairs of electron spins.

[7] At this point we repeat a remark in [1], in which we noticed that—though they have the dimension of temperature—spin temperatures often do not need to be interpreted as thermodynamic temperatures, as it is mostly sufficient to define them as parameters determining the value of the diagonal components of the density matrix.

We combine our expressions for the density matrix. Then

$$\rho_S^{\pm}(\omega,\Delta)\rho_I^{\pm} = \frac{1}{\Xi_S(\omega,\Delta)\Xi_I} \times \exp \mp \frac{1}{2}[\omega\alpha(\omega) - (\omega-\Delta)\alpha(\omega-\Delta) - \Delta\beta_{SS} + \omega_{0I}(\beta_{SS}-\beta_I)], \tag{87}$$

and upon its insertion in (77) and (78) and solving the results, we obtain relations between the inverse Zeeman temperature $\alpha(\omega)$, the inverse electron interaction temperature β_{SS} and the inverse nuclear spin temperature β_I that describe the stationary states towards which the CE branch and the TM branch tend.

For the CE branch we set $\Delta = \omega_{0I}$, and (87) simplifies to

$$\rho_S^{\pm}(\omega,\omega_{0I})\rho_I^{\pm} = \frac{1}{\Xi_S(\omega,\omega_{0I})\Xi_I} \times \exp \mp \frac{1}{2}[\omega\alpha(\omega) - (\omega-\omega_{0I})\alpha(\omega-\omega_{0I}) - \omega_{0I}\beta_I]. \tag{88}$$

We now define

$$P_Z(\omega) = \tanh\frac{1}{2}\omega\alpha(\omega), \tag{89}$$

which corresponds to the polarization of the electron spins with a resonance frequency $\omega \leqslant \omega_{0S}^i < \omega + \mathrm{d}\omega$ in the limit that their mutual interactions are negligibly small. Then, after some algebra we find

$$\frac{1}{\Xi_S(\omega,\Delta)\Xi_I}\left[\rho_S^{+}(\omega,\omega_{0I})\rho_I^{+} - \rho_S^{+}(\omega,\omega_{0I})\rho_I^{+}\right] \propto [1 - P_Z(\omega) - P_Z(\omega-\omega_{0I})]P_I - [P_Z(\omega) - P_Z(\omega-\omega_{0I})], \tag{90}$$

and the left hand side of (77) vanishes, if

$$P_I = \frac{\int_{-\infty}^{\infty}\mathrm{d}\omega\, g_i(\omega)g_i(\omega-\omega_{0I})[P_Z(\omega) - P_Z(\omega-\omega_{0I})]}{\int_{-\infty}^{\infty}\mathrm{d}\omega\, g_i(\omega)g_i(\omega-\omega_{0I})[1 - P_Z(\omega)P_Z(\omega-\omega_{0I})]}. \tag{91}$$

This is precisely the stationary state that we would have obtained using the scrambled states approach—for a comparison using the same notation, see [12], Chapter 8.

Upon inspection of (78) and (87) it is immediately seen that such a simple relation is not so easily obtained for the TM branch. Because the integral over Δ is limited to the intervals $-\omega_{0I} \leqslant \Delta \leqslant -\Delta_0$ and $\Delta_0 \leqslant \Delta \leqslant +\omega_{0I}$, such a relation may even depend on the nuclear Zeeman splitting and hence on the type of nuclear spin. A general treatment requires integration of triple spin flips in a model for spectral diffusion, such as presented in the next section using the high temperature approximation, or using the model presented in [27] extended with nuclear spins. In particular, contrary to the predictions of the fluctuating field approach [19,20,18,21], our treatment of TM does not trivially renders $\beta_{SS} = \beta_I$ in all conditions. The reason for this discrepancy is that we include the whole spectrum $g_D(D)$ in our calculations, while the fluctuating field approach only includes the component corresponding to $D = \omega_{0I}$. So the fluctuating field approach sets $\Delta = 0$ and (87) reduces to

$$\rho_S^{\pm}\rho_I^{\pm} = \frac{1}{\Xi_S(\omega,0)\Xi_I}\exp\left[\mp\frac{1}{2}\omega_{0I}(\beta_{SS}-\beta_I)\right], \tag{92}$$

while (78) reduces to

$$\exp\left[-\frac{1}{2}\omega_{0I}(\beta_{SS}-\beta_I)\right] - \exp\left[+\frac{1}{2}\omega_{0I}(\beta_{SS}-\beta_I)\right] = 0, \tag{93}$$

and $\beta_I = \beta_{SS}$ in the stationary state.

Still, also in our more general treatment there are at least two cases, in which the TM branch tends to a stationary state in which $\beta_{SS} = \beta_I$. First, 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 [14] and its extension beyond the high temperature approximation [28,27] predict that

$$\omega\alpha(\omega) - (\omega-\Delta)\alpha(\omega-\Delta) = \Delta\beta_{SS} \tag{94}$$

for all ω and Δ. Then again

$$\rho_S^{\pm}\rho_I^{\pm} = \frac{1}{\Xi_S(\omega,\Delta)\Xi_I}\exp\left[\mp\frac{1}{2}\omega_{0I}(\beta_{SS}-\beta_I)\right], \tag{95}$$

and again $\beta_I = \beta_{SS}$ in the stationary state. Notice that this expression still holds when $\Delta = \omega_{0I}$, so in this case also the CE branch tends to equalize β_I and β_{SS}.

The other case concerns nuclear spin-lattice relaxation, so no microwave field is present. Let us now suppose that this implies that the electron Zeeman temperature of all electron spins is equal to the lattice temperature T_L, but that the nuclear spin temperature T_I and the electron interaction temperature T_{SS} may differ from T_L. Then $\alpha(\omega)$ and $\alpha(\omega-\Delta)$ are equal to the inverse lattice temperature

$$\beta_L = \frac{\hbar}{k_B T_L} \tag{96}$$

for all frequencies ω, and

$$\begin{aligned}\widetilde{\rho}_S^{\pm\pm}(\omega,\Delta) &= \exp\mp\tfrac{1}{2}[2\omega-\Delta]\beta_L,\\ \widetilde{\rho}_S^{\pm}(\omega,\Delta) &= \exp\mp\tfrac{1}{2}[\Delta\beta_L + (\omega_{0I}-\Delta)\beta_{SS}].\end{aligned} \tag{97}$$

As a result

$$\rho_S^{\pm}(\omega,\Delta)\rho_I^{\pm} = \frac{1}{\Xi_S(\omega,\Delta)\Xi_I}\exp\mp\frac{1}{2}[\Delta(\beta_L-\beta_{SS}) + \omega_{0I}(\beta_{SS}-\beta_I)], \tag{98}$$

and again $\beta_I = \beta_{SS}$ in the stationary state. This is seen as follows. If we insert $\beta_I = \beta_{SS}$ in this expression for $\rho_S^{\pm}(\omega,\Delta)\rho_I^{\pm}$, the integrant in our condition (78) for the stationary state reduces to

$$\int_{-\infty}^{\infty}\mathrm{d}\omega\, g_i(\omega)g_i(\omega-\Delta)\sqrt{\omega_{0I}^2-\Delta^2}\,\tanh\left[-\frac{1}{2}\Delta(\beta_L-\beta_{SS})\right] \tag{99}$$

which is an uneven function of Δ, and hence the integral over Δ vanishes. Notice that this result suggests that during DNP the TM branch may still lead to $\beta_I \approx \beta_{SS}$ when spectral diffusion is so slow, that the microwave field only burns a narrow hole in the ESR signal.

In this case the CE branch differs from the TM branch. To obtain the stationary state to which the former branch tends we set $\Delta = \omega_{0I}$ in (98):

$$\rho_S^{\pm}(\omega,\Delta)\rho_I^{\pm} = \frac{1}{\Xi_S(\omega,\omega_{0I})\Xi_I}\exp\left[\mp\frac{1}{2}\omega_{0I}(\beta_L-\beta_I)\right], \tag{100}$$

which, upon insertion in (77), yields that the CE branch tends to a stationary state, in which $\beta_I = \beta_L$.

9. DNP in the high temperature approximation

As mentioned at the beginning of Section 7, for a complete description of DNP via the CE and TM we need to add the microwave field, spectral diffusion and electron spin lattice relaxation. This can be done analytically in the limit of the high temperature approximation, in which Boltzmann factors are expanded linearly. Then we can use Provotorov's equations for magnetic resonance saturation and cross relaxation [13,14] and combine them with the rate equations obtained here for triple spin flips. Such a treatment can be justified for DNP using e.g. electron spins with $g \approx 2$ in a static field of 3.4 T at temperatures above 4.2 K, so $\hbar\omega_{0S}/2k_BT < 0.54$. An extension beyond the high temperature approximation requires embedding the rate equations obtained above in numerical models for magnetic resonance saturation

and spectral diffusion as presented in [28,27]. This non-trivial extension will be described elsewhere.

Provotorov developed his theory of cross relaxation for spin systems with a discrete set of different Zeeman splittings. We first introduce the main components of his theory and next extend it to the continuous range of Zeeman splittings in our electron spin system. Thus we start considering a spin system containing two types of mutually interacting electron spins $S^i = \frac{1}{2}$ and $S^j = \frac{1}{2}$. It is subjected to an externally applied static magnetic field, a microwave field and spin-lattice relaxation. We describe it with the Hamiltonian

$$\mathcal{H} = \omega_{0S}\sum_i S_z^i + \omega'_{0S}\sum_j S_z^j + \mathcal{H}'_{SS} + \frac{1}{2}\sum_{i,j} D^{ij}_{+-}\left(S^i_+ S^j_- + S^i_- S^j_+\right) + 2\omega_{1S}\sum_i S^i_x \cos\omega t + \mathcal{H}_{SL}. \tag{101}$$

Here the first two terms represent the Zeeman interaction of the two types of electron spin with the externally applied static magnetic field. As usual the z-axis of the laboratory frame of reference is chosen parallel to this static field. The third term represent the truncated mutual interactions between the electron spins [22]. These first three terms lead to an ESR spectrum

$$g(\omega) = g_i h(\omega - \omega_{0S}) + g'_i h(\omega - \omega'_{0S}), \tag{102}$$

consisting of two lines with relative amplitudes g_i and g'_i and centred at the Zeeman splittings ω_{0S} and ω'_{0S}. These two lines are homogeneously broadened by $\mathcal{H}'_{SS}$, and $h(\Delta)$ is the resulting homogeneous lineshape. We characterize the latter by its moments

$$M_n = \int_{-\infty}^{\infty} \mathrm{d}\Delta\, \Delta^n h(\Delta) \tag{103}$$

and normalize $g(\omega)$ setting $M_0 = 1$ and $g_i + g'_i = 1$.

The remaining terms in the Hamiltonian (101) are non-diagonal on a basis of eigenstates of the first three terms. The first of these is the flip-flop term in the interaction between the two types of spin species and the cause of cross relaxation between these two types of electron spin. The next term originates in the interaction of the spins S^i with a microwave field $2B_1 \cos\omega_m t$ tuned to a frequency ω_m near their Zeeman splitting ω_{0S}. The final term represents the interaction of the two types of electron spin with the lattice vibrations.

Provotorov uses Zwanzig's perturbation method to solve the Liouville equation [29,25]. The first three terms of the Hamiltonian are then considered as the unperturbed part of the Hamiltonian and the remaining terms as perturbations causing the evolution of the part of the density matrix that is diagonal on a basis of eigenstates of the first three terms. This diagonal part is expanded up to first order in the high temperature approximation and written as

$$\rho = \frac{1}{\mathrm{Tr}\{1\}}\left(1 - \omega_{0S}\alpha\sum_i S_z^i - \omega'_{0S}\alpha'\sum_j S_z^j - \mathcal{H}'_{SS}\beta_{SS}\right). \tag{104}$$

Here α and α' are inverse electron Zeeman temperatures and β_{SS} is the inverse electron interaction temperature as defined in the previous section.

This density matrix enables the division of the expectation value of the unperturbed part of the Hamiltonian into three energy reservoirs: two electron Zeeman reservoirs containing the electron Zeeman energies

$$U_Z = -\frac{1}{2}N_S g_i \omega_{0S}^2 \alpha, \tag{105}$$

$$U'_Z = -\frac{1}{2}N_S g'_i (\omega'_{0S})^2 \alpha', \tag{106}$$

and the electron interaction reservoir containing the electron interaction energy

$$U_{SS} = -\frac{1}{4}N_S M_2 \beta_{SS}. \tag{107}$$

Thus the high temperature approximation leads to a one-to-one linear relation ship between the energies in these three reservoirs and the three inverse spin temperatures.

Finally, Provotorov derives a set of rate equations for the evolution of the three inverse spin temperatures due to the three non-diagonal contributions to the Hamiltonian (101):

$$\omega_{0S}\frac{\partial\alpha}{\partial t} = -\frac{\pi}{2}\omega_{1S}^2 h(\omega_m - \omega_{0S})[\omega_{0S}\alpha + (\omega_m - \omega_{0S})\beta_{SS}] - \frac{1}{T_{1S}}\omega_{0S}[\alpha - \beta_L] - \frac{\pi}{2}M_2 g'_i \times \int_{-\infty}^{\infty}\mathrm{d}\omega\, h(\omega)h(\omega_{0S} - \omega'_{0S} - \omega) \times [\omega_{0S}\alpha - \omega'_{0S}\alpha' - (\omega_{0S} - \omega'_{0S})\beta_{SS}], \tag{108}$$

$$\omega'_{0S}\frac{\partial\alpha'}{\partial t} = -\frac{1}{T_{1S}}\omega'_{0S}[\alpha' - \beta_L] + \frac{\pi}{2}M_2 g_i \times \int_{-\infty}^{\infty}\mathrm{d}\omega\, h(\omega)h(\omega_{0S} - \omega'_{0S} - \omega) \times [\omega_{0S}\alpha - \omega'_{0S}\alpha' - (\omega_{0S} - \omega'_{0S})\beta_{SS}], \tag{109}$$

$$M_2\frac{\partial\beta_{SS}}{\partial t} = -\frac{\pi}{2}\omega_{1S}^2 h(\omega_m - \omega_{0S})(\omega_m - \omega_{0S})[\omega_{0S}\alpha + (\omega_m - \omega_{0S})\beta_{SS}] - \frac{1}{T_{1SS}}M_2[\beta_{SS} - \beta_L] + \frac{\pi}{2}M_2 g_i g'_i \times \int_{-\infty}^{\infty}\mathrm{d}\omega\, h(\omega)h(\omega_{0S} - \omega'_{0S} - \omega) \times (\omega_{0S} - \omega'_{0S})[\omega_{0S}\alpha - \omega'_{0S}\alpha' - (\omega_{0S} - \omega'_{0S})\beta_{SS}]. \tag{110}$$

In these equations β_L is the inverse lattice temperature defined in (96), T_{1S} the spin-lattice relaxation time of the electron Zeeman energy, and T_{1SS} the spin-lattice relaxation time of the mutual interaction between the electron spins. Because the two electron Zeeman energies U_Z and U'_Z and the electron interaction energy U_{SS} are proportional to the inverse spin temperatures α, α' and β_{SS}, these rate equations directly provide the flows of energy in the spin system.

We continue extending Provotorov's theory of magnetic resonance saturation and cross relaxation to our spin system consisting of N_S randomly distributed and oriented electron spins $S = \frac{1}{2}$. Fig. 6 is a schematic representation of an ESR spectrum based on the electron spin part (2) of the unperturbed Hamiltonian. The dashed curve represents the inhomogeneous lineshape $g_i(\omega)$ and corresponds to the distribution of electron Zeeman splittings ω^i_{0S}. Thus, $g_i(\omega)\mathrm{d}\omega$ is the probability that $\omega \leqslant \omega^i_{0S} < \omega + \mathrm{d}\omega$. The drawn curves represent the homogeneous line shape $h(\omega)$ and corresponds to broadening of the spectrum due to the mutual interaction between the electron spins. Thus, $h(\Delta)\mathrm{d}\Delta$ is the probability that the mutual interaction between electron spins shifts the resonance frequency of an electron spin further by an amount between Δ and $\Delta + \mathrm{d}\Delta$. The full ESR lineshape is the convolution

$$g(\omega) = \int_{-\infty}^{\infty}\mathrm{d}\omega'\, g_i(\omega')h(\omega - \omega') \tag{111}$$

of the inhomogeneous and homogeneous lineshapes.

As mentioned above, Provotorov's theory of cross relaxation treats spin systems with a finite number of different Zeeman splittings. We extend this treatment to a continuous distribution of inequivalent spin species. As in the previous section we describe the state of the electron spins with a Zeeman splitting $\omega \leqslant \omega^i_{0S} < \omega + \mathrm{d}\omega$ with an inverse electron Zeeman temperature

$\alpha(\omega)$ and an inverse electron interaction temperature β_{SS}—which is the same for all electron spins. Then, in the high temperature approximation the total Zeeman energy of these electron spins is equal to

$$U_Z(\omega)\mathrm{d}\omega = -\frac{1}{2}N_S g_i(\omega)\omega^2\alpha(\omega)\mathrm{d}\omega, \tag{112}$$

while the total electron interaction energy is again given by (107). Furthermore, in this continuous limit the set of rate equations (108)–(110) is rewritten in the shape

$$\begin{aligned}\omega\frac{\partial\alpha(\omega)}{\partial t} = &-\frac{\pi}{2}\omega_{1S}^2 h(\omega_m-\omega)[\omega\alpha(\omega)+(\omega_m-\omega)\beta_{SS}]\\ &-\frac{1}{T_{1S}}\omega[\alpha(\omega)-\beta_L]-\frac{\pi}{2}M_2\int_{-\infty}^{\infty}\mathrm{d}\omega' g_i(\omega')\\ &\times\int_{-\infty}^{\infty}\mathrm{d}\omega''\,h(\omega'')h(\omega-\omega'-\omega'')\\ &\times[\omega\alpha(\omega)-\omega'\alpha(\omega')-(\omega-\omega')\beta_{SS}],\end{aligned} \tag{113}$$

$$\begin{aligned}M_2\frac{\partial\beta_{SS}}{\partial t} = &-\frac{\pi}{2}\omega_{1S}^2\int_{-\infty}^{\infty}\mathrm{d}\omega\, h(\omega_m-\omega)(\omega_m-\omega)[\omega\alpha(\omega)+(\omega_m-\omega)\beta_{SS}]\\ &-\frac{1}{T_{1SS}}M_2[\beta_{SS}-\beta_L]+\frac{\pi}{2}M_2\int_{-\infty}^{\infty}\mathrm{d}\omega g_i(\omega)\int_{-\infty}^{\infty}\mathrm{d}\omega g_i(\omega')\\ &\times\int_{-\infty}^{\infty}\mathrm{d}\omega''\,h(\omega'')h(\omega-\omega'-\omega'')\times(\omega-\omega')\\ &\times[\omega\alpha(\omega)-\omega'\alpha(\omega')-(\omega-\omega')\beta_{SS}].\end{aligned} \tag{114}$$

For the description of DNP we need to add the nuclear spins. As before we consider N_I equivalent nuclear spins $I=\frac{1}{2}$ with a Zeeman interaction (3) with the externally applied magnetic field. In the high temperature approximation the density matrix describing the state of these nuclear spins is approximated as

$$\rho_I = -\frac{1}{\mathrm{Tr}\{1\}}(1-\mathcal{Z}_I\beta_I). \tag{115}$$

As a result the nuclear spin polarization

$$P_I = \frac{1}{N_I I}\frac{1}{\mathrm{Tr}\{\rho\}}\sum_k^{N_I}\mathrm{Tr}\left\{\rho I_z^k\right\} = \frac{1}{2}\omega_{0I}\beta_I \tag{116}$$

is simply proportional to the inverse nuclear spin temperature β_I. We rewrite the rate equation (43) for the evolution of P_I as a rate equation for the evolution of β_I. On the left hand side we insert the expression for P_I given above. To rewrite the right hand side we notice that in the high temperature approximation (87) reduces to

$$\rho_S^{\pm}(\omega,\Delta)\rho_I^{\pm} = \pm\frac{1}{8}[\omega\alpha(\omega)-(\omega-\Delta)\alpha(\omega-\Delta)-\Delta\beta_{SS}+\omega_{0I}(\beta_{SS}-\beta_I)]. \tag{117}$$

We also insert (43) for the rate $W_{SSI}(\Delta)$. Thus we find a linear differential equation for the evolution of the inverse nuclear spin temperature:

$$\begin{aligned}\frac{\partial\beta_I}{\partial t} = &-\frac{\pi}{4}\frac{N_S}{N_I}\frac{A^2}{\omega_{0I}^2}\left[\int_{-\omega_{0I}}^{-\Delta_0}\mathrm{d}\Delta+\int_{\Delta_0}^{\omega_{0I}}\mathrm{d}\Delta\right]\int_{-\infty}^{\infty}\mathrm{d}\omega\, g_i(\omega)g_i(\omega-\Delta)\\ &\times\sqrt{\omega_{0I}^2-\Delta^2}\,g_D\left(\sqrt{\omega_{0I}^2-\Delta^2}\right)\\ &\times[\omega\alpha(\omega)-(\omega-\Delta)\alpha(\omega-\Delta)-\Delta\beta_{SS}+\omega_{0I}(\beta_{SS}-\beta_I)],\end{aligned} \tag{118}$$

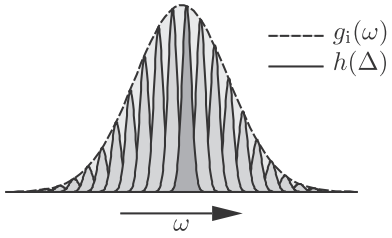

Fig. 6. Schematic representation of the structure of the ESR spectrum. The dashed curve represents the inhomogeneous lineshape $g_i(\omega)$, which corresponds to the distribution of electron Zeeman splittings. The drawn curves represent the homogeneous line shape $h(\Delta)$ and corresponds to broadening of the spectrum due to the mutual interaction between the electron spins.

in which—as before—the integration limit $\Delta_0 = \sqrt{\omega_{0I}^2 - D_0^2}$ if $D_0 < \omega_{0I}$ and $\Delta_0 = 0$ otherwise.

The evolution of β_I described by this rate equation includes two flows of energy: the CE flow between the nuclear Zeeman reservoir and the continuum of electron Zeeman reservoirs and the TM flow between the nuclear Zeeman reservoir and the electron interaction reservoir. As depicted in Figs. 4 and 5, the main effect of the CE on the electron Zeeman reservoirs is a flow of energy between electron spins with Zeeman splittings separated by the NMR frequency ω_{0I}. Thus it contributes to spectral diffusion. Estimates—see e.g. [12], Chapter 8—indicate that this contribution is still much smaller than spectral diffusion itself and we will ignore the effect of the CE on the evolution of the energy in the electron Zeeman reservoirs and hence of the inverse electron Zeeman temperatures $\alpha(\omega)$.

On the other hand, the change (60) of the electron interaction energy due to TM can be considerable. We insert (107) on the left hand side and (117) on the right hand side. We furthermore approximate the transition rate setting $D_D^2 \approx 0$ in the denominator of $g_D\left(\sqrt{\omega_{0I}^2-\Delta^2}\right)$, so (62) simplifies to

$$\frac{\omega_{0I}^2-\Delta^2}{\omega_{0I}^2}W_{SSI}(\Delta) \approx \frac{1}{2}\frac{A^2 D_D}{\omega_{0I}^3}\sqrt{\omega_{0I}^2-\Delta^2}. \tag{119}$$

As a result, after dividing both sides by $-\frac{1}{4}N_S$, we find

$$\begin{aligned}M_2\left(\frac{\partial\beta_{SS}}{\partial t}\right)_{TM} = &\frac{A^2 D_D}{\omega_{0I}^2}\left[\int_{-\omega_{0I}}^{-\Delta_0}\mathrm{d}\Delta+\int_{\Delta_0}^{\omega_{0I}}\mathrm{d}\Delta\right]\sqrt{\omega_{0I}^2-\Delta^2}\\ &\times\int_{-\infty}^{\infty}\mathrm{d}\omega\, g_i(\omega)g_i(\omega-\Delta)\\ &\times[\omega\alpha(\omega)-(\omega-\Delta)\alpha(\omega-\Delta)-\Delta\beta_{SS}+\omega_{0I}(\beta_{SS}-\beta_I)],\end{aligned} \tag{120}$$

in which, as above, the integration limit $\Delta_0 = \sqrt{\omega_{0I}^2 - D_0^2}$ if $D_0 < \omega_{0I}$ and $\Delta_0 = 0$ otherwise. We add the additional rate equation (118) to the set (113) and (114) and add this term to the latter. Thus we have obtained a closed set of rate equations for the inverse spin temperatures $\alpha(\omega)$, β_{SS} and β_I, from which the evolution of β_I—and hence of the nuclear spin polarization—during DNP can be solved.

Notice that the thus derived set of equations considers one type of nuclear spin only. Thus it does not yet differentiate between local and bulk nuclear spins separated by a diffusion barrier. Implementing this separation, as well as adding more types of nuclear spin is straightforward however. Moreover, also terms due transitions originating in the solid effect can be easily added using Abragam and Borghini's treatment [30].

10. Discussion and conclusions

The previous article [1] considered a model system consisting of a pair of interacting electron spins S^i and S^j and a single nuclear spin I^k and treated triple spin flips induced by the mutual interaction between the two electron spins together with the hyperfine or super-hyperfine interaction between one of the electron spins and the nuclear spin. While the scrambled states approach, which treats such triple spin flips by second order perturbation theory, can only be used when the mutual interaction between the two electron spins is small compared to the nuclear Zeeman splitting, so $|D^{ij}_{+-}| \ll \omega_{0I}$, the treatment given in the previous paper uses the exact eigenstates of the two interacting electron spins and calculates the transition rate with first order perturbation theory. Thus the results are valid for all values of D^{ij}_{+-}. It was shown that triple spin flips—in a single quantum mechanical transition—not only induce a flow of electron Zeeman energy to the nuclear spins, but also a flow of electron interaction energy to the nuclear spins. For $|D^{ij}_{+-}| \leqslant \omega_{0I}$ the two flows—which we denote as the cross effect (CE) and thermal mixing (TM) respectively—are proportional to

$$\frac{\omega_{0I}^2 - \left(D^{ij}_{+-}\right)^2}{\omega_{0I}^2} \quad \text{and} \quad \frac{\left(D^{ij}_{+-}\right)^2}{\omega_{0I}^2}, \tag{121}$$

while for $|D^{ij}_{+-}| > \omega_{0I}$ the two flows vanish.

The present paper extends the treatment to a system consisting of N_S randomly distributed and oriented electron spins with anisotropic g-tensors and N_I equivalent nuclear spins. As the previous paper it uses Zwanzig's perturbation expansion of the Liouville equation up to first order. In the extension the unperturbed density matrix includes pairs of interacting electron spins only. It is assumed that the concentration of electron spins is sufficiently low, and that their distribution is sufficiently random, so triples and larger clusters of interacting electron spins can be ignored. As a result the rate equations for all possible pairs of electron spins can simply be added. It should be noted, however, that some radicals may tend to assemble in clusters more easily than expected statistically. The dependence on concentration of the electron spin-lattice relaxation rate of trityls in a glass of glycerol:water can be explained assuming that trityls tend to assemble in clusters [31]. As an analytical treatment including larger clusters than pairs may turn out to be cumbersome, it may then be more profitable to resort to numerical models of clusters of electron spins as presented by e.g. Caracciolo et al. [32] and Kundu et al. [33].

In order to replace sums over electron spins by integrals, a distribution function $g_D(D)$ is introduced for the mutual interaction between the electron spins. This distribution function assumes the part of the spectrum of fluctuations in the fluctuating field approach. Notice that $g_D(D)\mathrm{d}D$ is not the probability that $D \leqslant D^{ij}_{+-} < D + \mathrm{d}D$, but rather the probability that the x and y-components of the local field experienced by the electron spins due their interaction with all other electron spins lie in the range between $\gamma_S^{-1}D$ and $\gamma_S^{-1}(D + \mathrm{d}D)$. The assumption that the electron spins are randomly distributed and oriented, leads to a Lorentzian shape of $g_D(D)$ cut-off at D_0, which is the maximum possible value of $|D^{ij}_{+-}|$ corresponding to the minimum possible distance between electron spins.

It is found that the relative strength of the two flows of energy—the TM flow of electron interaction energy to the nuclear spins and the CE flow of electron Zeeman energy to the nuclear spins—is determined by the ratio D_0/ω_{0I} of the cut-off frequency D_0 of the distribution function $g_D(D)$ and the nuclear Zeeman splitting ω_{0I}. For $D_0/\omega_{0I} \geqslant 1$ the rates of the two flows are equal. For $D_0/\omega_{0I} < 1$ the rate of the TM flow becomes gradually smaller than the rate of the CE flow, and for $D_0/\omega_{0I} \ll 1$ only the CE flow remains.

Now the cut-off frequency D_0 is completely determined by the radicals providing the electron spins and independent of the nuclear spins surrounding them. So, once a sample has been prepared, the relative strength of the two flows is the same for equivalent nuclear spins. On the other hand the relative contribution of the TM flow is larger for nuclear spins with a smaller NMR frequency—like e.g. ^{13}C spins—and smaller for those with a larger NMR frequency—like e.g. proton spins. It may even happen that there is a significant TM flow to the former type of nuclear spin while this flow is completely quenched for the latter type of nuclear spin—as is e.g. the case when $\omega_{0I}(^{13}\mathrm{C}) < D_0 \ll \omega_{0I}(^{1}\mathrm{H})$. On the other hand—with the exception of some local nuclear spins with resonance frequencies shifted significantly by strong hyperfine interaction—the ratio between TM and the CE flows of energy is the same for local nuclear spins near the electron spins as for the bulk nuclear spins further away.

The CE flow of electron Zeeman energy to the nuclear spins is found to be dominated by weakly interacting pairs of electron spins obeying the matching condition $\omega^i_{0S} - \omega^j_{0S} \approx \omega_{0I}$. As a result this flow leads to the same stationary state as obtained by the scrambled states approach as introduced by Kessenikh [15]. For small values of the cut-off frequency D_0 the rate of this flow is also the same as obtained by the scrambled states approach. However, for larger values of D_0 this rate is found to be smaller. This reduction has a simple origin: conservation of energy inhibits pairs of electron spins, for which $D^{ij}_{+-} > \omega_{0I}$, to participate in triple spin flips. On the other hand the whole spectrum $g_D(D)$ is found to contribute to TM. As a result the transition rate for TM is not exactly equal to the rate determined with the fluctuating field approach, which only accounts for the component of the spectrum corresponding to $D \approx \omega_{0I}$.

It is seen that the cut-off frequency D_0 is a crucial parameter for the determination of the energy flows during DNP. Notice first that the cut-off frequency D_0 is determined by the smallest possible distance of the electron spins in nearest neighbour pairs. Thus D_0 will not only differ for different types of radical providing the electron spins, but may also depend on the host material. On the other hand the concentration of electron spins may not play a crucial part.

An issue to consider is that for real samples D_0 may differ significantly from its value as defined above. When, as noted above radicals tend to assemble in clusters, the shape of the distribution function $g_D(D)$ may change significantly and the cut-off frequency may be considerable larger, especially if these radicals tend to stack on top of each other in a preferred direction, so the their g-tensors coincide. For small or flat radicals it is also conceivable that the wave function of the unpaired electron spin extends to the edge of the molecule. Then the wave functions of the unpaired electron spins on nearest neighbour radicals may overlap, which leads to a contact or exchange interaction. This will also change the shape of $g_D(D)$, and, depending on the configuration, this may lead to an increase or a decrease of the cut-off frequency D_0. As mentioned above, an analytical treatment including such larger clusters may turn out to be cumbersome. Including exchange interactions may complicate the treatment even further, and in such cases it may be more profitable to resort to numerical models of clusters of electron spins as presented in [32,33].

Possibly ESR might provide an experimental value of D_0. Chen et al. discuss double quantum transitions of pairs of electron spins in a glass of glycerol:water doped with trityls, that may yield such an experimental value [31]. DNP experiments on samples, in which more than one nuclear spin species is present, may also provide an indication of the value of D_0. In such samples TM provides a mech-

anism for an exchange of energy between the various nuclear spin species. Kaminker et al. studied DNP of proton and deuterium spins in a glass of 50% $^{1,2}H_2O$/dimethyl sulfoxyde doped with 40 mM TEMPOL providing the electron spins [34]. Experiments performed at 6 K and 3.4 T yielded equal spin temperatures for the proton and deuterium spins in the stationary state after applying the microwave field for a long time. Electron-electron double resonance (ELDOR) performed on the same sample showed that the microwave field only burns a narrow hole in the ESR signal. This can be explained by TM as discussed above: if only a narrow hole is burnt in the ESR signal, for most electron spins the inverse electron Zeeman temperature $\alpha(\omega)$ is equal to the inverse lattice temperature β_L. As discussed in Section 8, TM may then tend to a stationary state, in which the inverse electron interaction temperature β_{SS} is approximately equal to the inverse nuclear spin temperature β_I. As this applies for all nuclear spin species in the sample, all these spin species should reach approximately the same inverse spin temperature.

This observation is supported by Capozzi, who studied DNP of proton and ^{13}C spins in glasses of sodium [1-^{13}C]acetate dissolved in a water:glycerol solution with different degrees of deuteration and doped with 50 mM TEMPOL [35]. Experiments performed at 1.5 K and 3.4 and 5 T also yielded equal inverse nuclear spin temperatures for the proton and ^{13}C spins in the stationary state reached after applying the microwave field for a long time. However, upon increasing the magnetic field to 7 T, these two nuclear spin species reached different inverse spin temperatures. This indicates that the cut-off frequency D_0 is significantly smaller than the NMR frequency $\omega_{0I}/2\pi = 299$ MHz in this specific case. As an appreciable energy flow due to TM still occurs down to $D_0/\omega_{0I} \approx 0.5$, these experiments suggest that the cut-off frequency is probably lower than 150 MHz.

Also Guarin et al. observed the breakdown of equal inverse nuclear spin temperatures at such a high magnetic field [36]. Among other materials they studied DNP of proton spins and ^{13}C spins in glasses of [1-^{13}C]pyruvate dissolved in a D_2O:H_2O:glycerol-d8 solution, also doped with TEMPOL, now at concentrations varying from 10 to 100 mM. In experiments at 4.2 K and 6.7 T the stationary state after applying the microwave field for a long time exhibited equal inverse spin temperatures for the higher concentrations of 50 and 100 mM, but not anymore for the lower concentrations of 40, 25 and 10 mM. This suggest that the cut-off frequency may be larger than 0.5 ω_{0I}—which corresponds to 143 MHz for proton spins—for higher concentrations, possibly due to clustering of the TEMPOL molecules. Such clustering would explain the observed concentration dependence of the electron spin-lattice relaxation rate of TEMPO in a glass of butanol [37] in the same way as it explained it for trityl in a glass of glycerol:water [31].

In a second experiment, similar to the early experiment of Cox et al. [2], the nuclear spins were first polarized by DNP. Next the polarization of the ^{13}C spins was reduced to zero by means of a series of saturating RF pulses. Subsequently this polarization was monitored by NMR. At all concentrations of TEMPOL the polarization of the ^{13}C spins was seen to recover. As this recovery can be explained by a TM flow of energy from the deuterium spins to the ^{13}C spins, this experiment does not contradict the observation that the cut-off frequency is much lower than the NMR frequency of the proton spins. On the other hand, as an appreciable energy flow due to TM still occurs at $D_0/\omega_{0I} \approx 0.5$, and $\omega_{0I}/2\pi = 72$ MHz at 6.7 T, this indicates that $D_0/2\pi \gtrsim 35$ MHz, even at such a low concentration of TEMPO that triples and larger clusters of electron spins can be ignored.

It may be useful to consider samples, in which the minimum distance between radicals can be engineered. This can be done by either doping materials with more than one radical sub-group [38,39]—so the distance between electron spins is known more precisely—or by embedding a radical in a larger molecule—so their minimum distance is larger, and thus the cut-off frequency D_0 is reduced.

The treatment presented here excludes broadening of the ESR spectrum by the terms $D^{ij}_{zz}S^i_zS^j_z$ in the hyperfine and super-hyperfine interaction. In triple spin flips involving two electron spins S^i and S^j and a nuclear spin I^k, the expectation value of $D^{ij}_{zz}S^i_zS^j_z$ does not change, so this term does not contribute to the energy flows. However the expectation value Δ^{ij}_{SS} of the terms $D^{il}_{zz}S^i_zS^l_z$ and $D^{jl}_{zz}S^j_zS^l_z$ in the interaction of S^i and S^j with other spins S^l does change. As a result the CE flow of energy—as derived in this paper—is not anymore a pure transfer of electron Zeeman energy to the nuclear spins, but also involves some transfer of electron interaction energy. This flow of electron interaction energy to or from the nuclear spins was recently studied by Karabanov et al. for mainly homogeneously broadened ESR spectra, such that Δ^{ij}_{SS} is comparable to or larger than the difference $\omega^i_{0S} - \omega^j_{0S}$ of the electron Zeeman splittings [23]. Then the fraction of electron interaction energy in the flow can be considerable.

In our case of mainly inhomogeneously broadened ESR spectra, such that $\omega^i_{0S} - \omega^j_{0S}$ is on average much larger than Δ^{ij}_{SS}, this contribution to the flow of electron interaction energy is much smaller than the flow due to the TM branch as calculated in this article. To keep the argument simple, we illustrate this using the high temperature approximation and assuming fast spectral diffusion, so (94) holds for all pairs of electron spins. Then it can be inferred from the treatment in the previous paper [1], that a single triple spin flip with S^i and S^j changes the Zeeman energy of I^k on average by an amount

$$\frac{1}{4}\omega^2_{0I}(\beta_{SS} - \beta_I). \tag{122}$$

We determine the fraction of this energy originating in the electron interaction energy due to homogeneous broadening. In the high temperature approximation the probability that Δ^{ij}_{SS} has a value Δ_{SS} is equal to $1 - \frac{1}{2}\Delta_{SS}\beta_{SS}$. Furthermore, the distribution of the values of Δ_{SS} is the convolution

$$g_{SS}(\Delta_{SS}) = \int_{-\infty}^{\infty} \mathrm{d}\omega\, h(\omega)h(\Delta_{SS} - \omega) \tag{123}$$

of the homogeneous lineshape with itself. Hence, on average a triple spin flip changes the electron interaction energy by an amount

$$\frac{1}{2}(\beta_{SS} - \beta_I)\int_{-\infty}^{\infty} \mathrm{d}\Delta_D\, \Delta_D^2 g_{SS}(\Delta_D) \tag{124}$$

As discussed in Appendix A we can equate the homogeneous lineshape with the distribution function $g_D(D)$. This is a Lorentzian, and the second moment of the convolution of a Lorentzian with itself is twice the second moment of that Lorentzian. Then, using (A.8) we find that the fraction of electron interaction energy transferred by the CE branch of energy transfer is equal to

$$\frac{4M_2}{\omega^2_{0I}} = \frac{8}{\pi}\frac{D_0 D_D}{\omega^2_{0I}}. \tag{125}$$

We compare this ratio with (70) and notice that $D_D \ll D_0$ for dilute electron spin systems. We see that for inhomogeneously broadened ESR spectra this contribution to the transfer of electron interaction energy is much smaller than the contribution of the TM branch as determined in the present article.

TM involving the local nuclear spins near the electron spins may be fast, and, as already noticed by Cox et al. [2], it then couples the mutual interactions between the electron spins and the Zeeman

energy of the local nuclear spins near the electron spins into a single energy reservoir. If the rate of nuclear spin diffusion is sufficiently fast, the energy of the bulk nuclear spins is also contained in this joint reservoir. As a result TM may influence the results of electron spin double resonance (ELDOR) experiments. In these experiments a short microwave pulse is used to burn a narrow hole in the ESR signal. Then after a short time the ESR signal is monitored in order to determine the broadening of that hole due to spectral diffusion. Recall that spectral diffusion is caused by flip-flop transitions between electron spins S^i and S^j with different Zeeman splittings ω_{0S}^i and ω_{0S}^j, and that the energy $\pm\left(\omega_{0S}^i - \omega_{0S}^j\right)$ needed for these transitions is provided by the electron interaction reservoir. As the amount of energy that can be stored in this reservoir is small, the result is expected to be a gradient of electron spin polarization across the ESR spectrum instead of complete saturation of all polarization [14]. However, if TM combines the electron interaction energy with the Zeeman energy of the local nuclear spins into a single reservoir, the resulting reservoir may be sufficiently large to supply the necessary energy. Hence, on the short time scale of ELDOR experiments conservation of energy is a lesser issue, and one may not observe the polarization gradient predicted by Provotorov's theory.

We recall our remark made in the previous paper [1] that coherent effects may be involved in the energy transfer when the hyperfine or super-hyperfine interaction is strong, i.e. in the transfer of energy to the local nuclear spins. However, precisely because the energy of these local nuclear spins may be contained in the same energy reservoir as the electron interaction energy, such coherent effects may be hard to detect.

The nuclear Zeeman energy is determined by a single parameter: the inverse nuclear spin temperature β_I. On the other hand, beyond the high temperature approximation the electron interaction energy is determined by two parameters: the inverse electron Zeeman temperature $\alpha(\omega)$ and the inverse electron interaction temperature β_{SS}. The fluctuating field approach finds that TM tends to render $\beta_I = \beta_{SS}$, because it assumes that TM is solely caused by the component $D = \omega_{0I}$ of the distribution function $g_D(D)$. Our approach includes the whole spectrum $g_D(D)$ in its treatment of TM, and, as a result, we find that TM does not trivially tends to equalize β_I and β_{SS}. In two cases we still find $\beta_I = \beta_{SS}$ however: first when spectral diffusion across the ESR spectrum is fast and secondly when no microwave field is present, so $\alpha(\omega) = \beta_L$. The latter suggests that still $\beta_I \approx \beta_{SS}$, when spectral diffusion is slow, and the microwave field only burns a narrow hole in the ESR signal.

Future work will focus on integrating triple spin flips in the model for spectral diffusion presented in [27], thus extending the treatment of DNP in Section 9 to beyond the high temperature approximation, so comparison with experiments at low temperature is possible. It should be noted that such comparisons are not trivial, because in addition to parameters like the rates of spin-lattice relaxation and spectral diffusion, now also the cut-off frequency D_0 of the distribution function $g_D(D)$ and the rates of nuclear spin diffusion have to be estimated or deduced from experiment.

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Appendix A. The distribution function $g_D(D)$

In this Appendix we derive an expression for the distribution function $g_D(D)$. For this purpose we consider the model system described in Section 2. It consists of N_S electron spins $S^i = \frac{1}{2}$ that are randomly distributed and oriented in a volume V. We assume that there exists a minimum distance r_0 between these electron spins, e.g. because the radicals providing them have a finite size. However, the system is dilute, and this minimum distance r_0 is at least an order of magnitude smaller than the average distance n_S^{-3}, where $n_S = N_S/V$. Their interaction is furthermore assumed to be purely dipolar. So for a pair of electron spins S^i and S^j separated by a vector $\mathbf{r}_{ij} = (r_{ij}, \theta_{ij}, \phi_{ij})$,

$$D_{+-}^{ij} = \frac{1}{2}\frac{\mu_0}{4\pi}\frac{\hbar\gamma_S^i\gamma_S^j}{r_{ij}^3}\left(1 - 3\cos^2\theta_{ij}\right). \tag{A.1}$$

Here γ_S^i and γ_S^j are the gyromagnetic ratios of the electron spins S^i and S^j and $\mu_0 = 4\pi \times 10^{-7}$ is the permeability of free space.[8] We make one further assumption: we assume that the width of the inhomogeneous lineshape is much smaller than the Zeeman splitting of the electron spins, as is generally the case for radicals used for DNP. This corresponds to assuming that the spread in values of γ_S^i and γ_S^j is much smaller than their average value

$$\gamma_S = \frac{1}{N_S}\sum_i^{N_S}\gamma_S^i. \tag{A.2}$$

This enables us to approximate $\gamma_S^i\gamma_S^j$ in our expression for D_{+-}^{ij} by its average γ_S^2.

In the text we introduce the distribution function $g_D(D)$ enabling the replacement of sums over S^i and S^j of functions $f\left(D_{+-}^{ij}\right)$ by an integral over $f(D)$:

$$\frac{1}{N_S}\sum_i^{N_S}\sum_{j\neq i}^{N_S} f\left(D_{+-}^{ij}\right) = \int_{-\infty}^{\infty} \mathrm{d}D\, f(D) g_D(D). \tag{A.3}$$

Our aim is to provide an analytic expression for this distribution function. From its definition follows that the moments of this distribution function are equal to

$$M_n = \frac{1}{N_S}\sum_i^{N_S}\sum_{j\neq i}^{N_S}\left(D_{+-}^{ij}\right)^n = \int_{-\infty}^{\infty}\mathrm{d}D\, D^n g_D(D) \tag{A.4}$$

To characterize $g_D(D)$ we only need its second moment. For its evaluation we approximate the sums over S^i and S^j by integrals:

$$\begin{aligned} M_2 &= \frac{1}{N_S}\sum_i^{N_S}\sum_{j\neq i}^{N_S}\left(\frac{1}{2}\frac{\mu_0}{4\pi}\frac{\hbar\gamma_S^2}{r_{ij}^3}\left(1 - 3\cos^2\theta_{ij}\right)\right)^2 \\ &\approx n_S\int_{r_0}^{\infty}\mathrm{d}r\, r^2 \\ &\quad\times\int_0^{2\pi}\mathrm{d}\phi\int_0^{\pi}\mathrm{d}\theta\,\sin\theta\left(\frac{1}{2}\frac{\mu_0}{4\pi}\frac{\hbar\gamma_S^2}{r^3}\left(1 - 3\cos^2\theta\right)\right)^2 \\ &= \frac{4\pi}{15}\frac{n_S}{r_0^3}\left(\frac{\mu_0}{4\pi}\hbar\gamma_S^2\right)^2. \end{aligned} \tag{A.5}$$

We factorize this expression into two components. As mentioned above, the radicals providing the electron spins have a finite size, so there exists a minimum distance r_0 between spins. As a result $|D_{+-}^{ij}|$ has a maximum value

$$D_0 = \frac{\mu_0}{4\pi}\frac{\hbar\gamma_S^2}{r_0^3}. \tag{A.6}$$

Furthermore the average value of D_{+-}^{ij} is equal to

[8] Notice also that D_{+-} is chosen to be a factor two smaller than e.g. in [12]. This enables us to write the expressions in this article a bit more concisely.

$$D_{\mathrm{av}} = \sqrt{\overline{\left(D^{ij}_{+-}\right)^2}} = \frac{1}{2}\frac{\mu_0}{4\pi} n_S \hbar \gamma_S^2 \left[\frac{1}{4\pi}\int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \mathrm{d}\theta \, \sin\theta \left(1-3\cos^2\theta\right)^2\right]^{1/2} = \frac{1}{\sqrt{5}}\frac{\mu_0}{4\pi} n_S \hbar \gamma_S^2, \tag{A.7}$$

which is $n_S/r_0^3\sqrt{5}$ smaller than D_0. We now define $D_D = \left(4\pi^2\sqrt{5}/30\right)D_{\mathrm{av}} = 0.9366 D_{\mathrm{av}}$. Then

$$M_2 = \frac{2}{\pi} D_0 D_D. \tag{A.8}$$

For DNP the concentration of electron spins is generally low—typically $1\cdot10^{19}$–$4\cdot10^{19}$ cm^{-3} (16–66 mM). Then D_D/D_0 is less than about 0.01 when the minimum distance between electron spins is 1 nm and even smaller when this distance is shorter. So always $D_D \ll D_0$ and (A.8) is in good approximation the second moment of a Lorentzian

$$g_D(D) = \frac{D_D}{\pi\left(D^2 + D_D^2\right)} \tag{A.9}$$

with a width D_D and cut-off at D_0. To show this we calculate,

$$\int_{-D_0}^{D_0} \mathrm{d}D\, D^2 \, \frac{D_D}{\pi\left(D^2+D_D^2\right)} = \frac{2}{\pi} D_D^2 \left[\frac{D_0}{D_D} - \arctan\left(\frac{D_0}{D_D}\right)\right] \approx \frac{2}{\pi} D_0 D_D. \tag{A.10}$$

This distribution function is similar to the homogeneous lineshape in the case that the latter is solely due to the mutual interaction between electron spins while their polarization is low—for a derivation along similar lines of that lineshape see [12], Chapter 3. In the case that the mutual interaction between the electron spins is purely dipolar, so $D^{ij}_{zz} = 2D^{ij}_{+-}$ for all pairs of electron spins, the distribution function $g_D(D)$ is even identical to the homogeneous lineshape in the limit of low electron spin polarization. In the fluctuating field approach the spectrum of the fluctuations is generally equated to the homogeneous lineshape. Thus, in our more general approach the distribution function $g_D(D)$ assumes the role of that spectrum of fluctuations.

Like the homogeneous lineshape, the distribution function $g_D(D)$ is a narrow function in typical conditions for DNP: samples containing electron spins with $g \approx 2$ at a concentration between $1\cdot10^{19}$ and $4\cdot10^{19}$ cm^{-3} (16 to 66 mM) and static magnetic fields of several tesla. Then $D_D/2\pi$ is found to lie in the range 0.2–0.8 MHz, which is several orders of magnitude smaller than the NMR frequency ω_{0I}.

Notice that the homogeneous lineshape $h(\Delta)$ is *not* defined such that $h(\Delta)\mathrm{d}\Delta$ is the probability that $\Delta \leqslant \frac{1}{2}D^{ij}_{zz} < \Delta + \mathrm{d}\Delta$. Rather $h(\Delta)\mathrm{d}\Delta$ is the probability that the z-component of the local field experienced by the electron spins due their interaction with all other electron spins lies in the range between $\gamma_S^{-1}\Delta$ and $\gamma_S^{-1}(\Delta + \mathrm{d}\Delta)$. Similarly the distribution function $g_D(D)$ is *not* defined such that $g_D(D)\mathrm{d}D$ is the probability that $D \leqslant D^{ij}_{+-} < D + \mathrm{d}D$. Rather $g_D(D)\mathrm{d}D$ is the probability that the x and y-components of the local field experienced by the electron spins due their interaction with all other electron spins lie in the range between $\gamma_S^{-1}D$ and $\gamma_S^{-1}(D + \mathrm{d}D)$. Notice also that the cut-off frequency D_0 of the distribution function $g_D(D)$ corresponds to the interaction between two nearest neighbour electron spins only. Hence extensions of $g_D(D)$ beyond D_0 due to triples and larger clusters of more strongly interacting electron spins are considered to be negligible in the derivation of $g_D(D)$ given in this Appendix.

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