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The principles of dynamic nuclear polarisation

Tom Wenckebach[*†]
Paul Scherrer Institut
E-mail: `tomwenckebach@yahoo.com`

Several mechanisms have been identified for the polarisation transfer from the electron spins to the nuclear spins in DNP. Unfortunately, these were designated variously, sometimes even confusingly. Different processes were sometimes given the same name and different names were occasionally given to the same process. Distinguishing the various mechanisms experimentally proved to be notoriously difficult, adding to the confusion. Trying to bring some order in the chaos, this paper presents a historical account of the theoretical developments, including a rough description of the various mechanisms and some proposals for unequivocal names for the various mechanisms and processes.

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[*] Speaker.

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1. Introduction

The mechanisms for DNP can be subdivided into two families. In one family, known as the *solid effect*, the polarisation transfer is achieved in a single step. The microwave field combines with the super-hyperfine interaction to induce so-called *forbidden transitions*, simultaneous flip-flop or flip-flip transitions of an electron spin and a nuclear spin,

$$\begin{aligned} |m_S,m_I\rangle &= \left|+\tfrac{1}{2},-\tfrac{1}{2}\right\rangle \leftrightarrow \left|-\tfrac{1}{2},+\tfrac{1}{2}\right\rangle \ , \\ |m_S,m_I\rangle &= \left|+\tfrac{1}{2},+\tfrac{1}{2}\right\rangle \leftrightarrow \left|-\tfrac{1}{2},-\tfrac{1}{2}\right\rangle \ , \end{aligned} \tag{1.1}$$

thus transferring polarisation from the former to the latter.

In the other family, to be denoted as *thermal mixing*, the transfer occurs in a two-step process. First, the microwave field flips electron spins in normal ESR transitions. Next, the super-hyperfine interaction and the mutual interaction between the electron spins combine to induce *triple spin flips*, in which two electron spins and a nuclear spin flip simultaneously:

$$\begin{aligned} |m_S,m'_S,m_I\rangle &= \left|+\tfrac{1}{2},-\tfrac{1}{2},-\tfrac{1}{2}\right\rangle \leftrightarrow \left|-\tfrac{1}{2},+\tfrac{1}{2},+\tfrac{1}{2}\right\rangle \ , \\ |m_S,m'_S,m_I\rangle &= \left|+\tfrac{1}{2},-\tfrac{1}{2},+\tfrac{1}{2}\right\rangle \leftrightarrow \left|-\tfrac{1}{2},+\tfrac{1}{2},-\tfrac{1}{2}\right\rangle \ . \end{aligned} \tag{1.2}$$

Also these triple spin flips transfer the polarisation from one of the two electron spins to the nuclear spins.

2. The Solid Effect

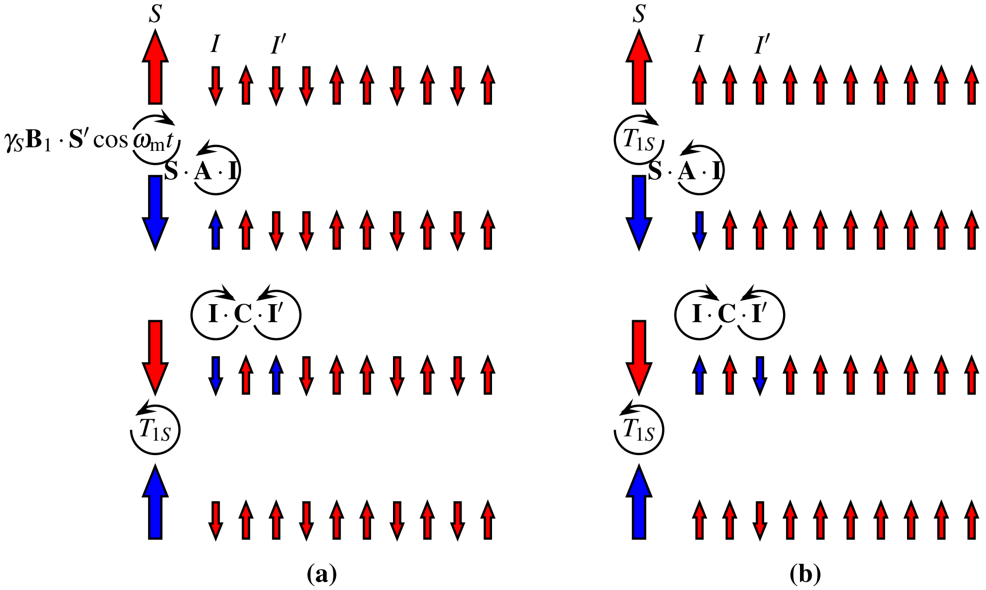

Figure 1: (a) Cartoon depicting the fundamental processes involved in DNP via the solid effect. (b) Cartoon depicting the fundamental processes involved in direct nuclear spin-lattice relaxation. For the explanation see the text.

The solid effect was first proposed by Jeffries [2] in 1957, and shortly afterwards, but independently by Übersfeld and coworkers [3] and Abragam and Proctor [4]. After preliminary studies by Jeffries and Abraham[1] [5, 6], the solid effect was used by Jeffries and co-workers to explain their early DNP experiments on $La_2Mg_3(NO_3)_{12}.24H_2O$ (LMN) doped with Ce^{3+} and Nd^{3+} [7, 8, 9, 10, 11].

A simple picture of the various processes playing a role in the solid effect is provided in Figure 1a. The big arrow represents an electron spin S and the small arrows some surrounding nuclear spins I, I', etc. The direction of the arrows corresponds to the polarisation of the spins. The top row shows the initial conditions. We start with a high electron spin polarisation P_S, so the big arrow points up, while the nuclear spin polarisation P_I is still low, so the small arrows are oriented randomly.

The aim of DNP is to polarise all nuclear spins, i.e., to point all small arrows in the same direction. To point them all up, the microwave frequency ω_m is tuned to the difference $\omega_S - \omega_I$ of the resonance frequencies of the electron spin S and a nearby nuclear spin I. Then the super-hyperfine interaction $\mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I}$ and the microwave field cooperate to flip these two spins simultaneously. Such combined spin flips are known in the literature as *forbidden transitions*, though it would be more appropriate to denote them as *second order transitions*. As seen in the second row, the polarisation of the electron spin is transferred to the nearby nuclear spin. Subsequently the resulting nuclear spin polarisation needs to be transported to the nuclear spins further away. The third row shows, how flip-flop transitions

$$|m_I, m_I'\rangle \;=\; \left|+\tfrac{1}{2}, -\tfrac{1}{2}\right\rangle \leftrightarrow \left|-\tfrac{1}{2}, +\tfrac{1}{2}\right\rangle \;, \tag{2.1}$$

induced by the mutual interaction $\mathbf{I}\cdot\mathbf{C}\cdot\mathbf{I}'$ between the nuclear spins take care of this transport. This process is known as *nuclear spin diffusion*. Finally the electron spin S flips back via electron spin-lattice relaxation, so the whole process can start all over again and more nuclear spins can be polarised.

The fundamental process of the solid effect is the simultaneous transition of an electron spin and a nuclear spin leading from the first to the second row. This transition needs to conserve energy. So the matching condition

$$\omega_S = \omega_\mathrm{m} \pm \omega_I \tag{2.2}$$

must hold in order to transfer polarisation from the electron spins to the nuclear spins. In Figure 1a this condition holds with the + sign. There down-pointing small arrows are flipped upwards, so positive polarisation is transferred to the nuclear spins. When the matching condition holds with the − sign, up-pointing small arrows are flipped downwards, so negative polarisation is transferred instead. We now distinguish two varieties of the solid effect. The first variety is denoted as the *well-resolved solid effect*. It occurs when the ESR spectrum is narrow, and it width is smaller than the resonance frequency ω_{0I} of the nuclear spins. Then, for some microwave frequencies the matching condition can hold with the + sign and for some other microwave frequencies with − sign. But the matching condition can never hold with the + sign and the − sign simultaneously. So either only positive polarisation is transferred, or only negative polarisation.

The other variety of the solid effect occurs when the ESR spectrum is broad, and their width is of the same order of magnitude as ω_{0I}. Then, for some microwave frequencies there may be electron spins obeying the matching condition with the + sign, as well as electron spins obeying the

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[1] M. Abraham, not to be confused with Anatole Abragam. Surprisingly, in his second paper the former does not refer to his earlier paper with Jeffries.

matching condition with the $-$ sign. As a result, positive and negative polarisation are transferred simultaneously and the net transfer is the difference between the two. Moreover, the microwave field also saturates electron spins with a resonance frequency $\omega_S \approx \omega_\mathrm{m}$. If spectral diffusion is slow, the microwave field only burns a hole in the ESR signal and the electron spins obeying the matching condition $\omega_S = \omega_\mathrm{m} \pm \omega_I$ are not affected. This variety is known as the *differential solid effect*.

If, however, spectral diffusion is fast, the saturation of the electron spins with a resonance frequency $\omega_S \approx \omega_\mathrm{m}$ spreads to the electron spins obeying the matching condition $\omega_S = \omega_\mathrm{m} \pm \omega_I$. Then we need Provotorov's theory to describe the evolution of the polarisation of these electron spins. Abragam and co-workers developed the theory of the solid effect for this case (for a review see [12]). Their description does not yet include thermal mixing, but leads to a very similar behaviour of the nuclear spin polarisation. Because of the similarity, this mechanism is best denoted as *Microwave Induced Thermal Mixing*, but notice that it belongs to the family of the solid effect and *not* to the family of Thermal Mixing.

Let us return to the fundamental process of the solid effect: the second order transition of an electron spin and a nuclear spin leading from the first row to the second row in Figure 1a. It needs the simultaneous action of two interactions, the super-hyperfine interaction and the interaction of the electron spins with the microwave field. There are several approaches to treat such second order transitions, all leading to the same result. In his description of the solid effect Jeffries used the *scrambled state* approach [2, 7, 9]. Then one considers the electron spin states and the nuclear spin states to be mixed by the terms $A_{z\pm} S_z I_\mp$ in super-hyperfine interaction. The microwave field induces transitions between these mixed states, thus causing an electron spin and a nuclear spin to flip simultaneously. Unfortunately this approach is restricted to weak microwave fields.

This restriction is overcome, using an *alternative scrambled state* approach, where one considers the up and down states of the electron spin to be mixed by the microwave field, while the super-hyperfine interaction induces transitions between these mixed states. In this alternative scrambled state approach the mixing of the up and down states of the electron spin can be calculated exactly, while the original scrambled state approach is confined to perturbation methods. As a result this approach is not restricted to weak microwave fields. This advantage is exploited to its full extend in the theory of pulsed DNP methods like *nuclear orientation via electron spin locking* (NOVEL) and the *integrated solid effect* (ISE) [13, 14]. For further details, see the contribution of Hautle to these proceedings and references therein [15].

3. Direct Nuclear Spin-Lattice Relaxation

It would be great, if after DNP all nuclear spins were to stay polarised forever, so we could use these polarised spins all the time required by our applications. But the very electron spins, that we need to polarise the nuclear spins with DNP, also destroy the nuclear spin polarisation by means of nuclear spin-lattice relaxation. There are two channels through which this nuclear spin-lattice relaxation can take place. One, to be called here *direct nuclear spin-lattice relaxation*, is related to the solid effect and is the subject of this section. The other involves thermal mixing and is postponed to the following section.

A simple picture of the various processes playing a role in direct nuclear spin-lattice relaxation is provided by Figure 1b. As in Figure 1a, the big arrow represents the polarisation of an electron spin S and the small arrows the polarisation of some surrounding nuclear spins I, I', etc. Again the top row shows the initial conditions. This time we assume, that we have successfully polarised the nuclear spins, so all small arrows point up.

The electron spin-lattice interaction flips the big arrow between up and down with the electron spin-lattice relaxation rate T_{1S}^{-1}. Every once in a while, the electron spin-lattice interaction combines with the super-hyperfine interaction $\mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}$ and flips both an electron spin and a nearby nuclear spin. As seen in the second row, this transfers the polarisation from this nearby nuclear spin back to the electron spin. Subsequently the mutual interaction $\mathbf{I} \cdot \mathbf{C} \cdot \mathbf{I}'$ between the nuclear spins induces flip-flop transitions, spreading this loss of polarisation to the nuclear spins further away. As the electron spin continues flipping up and down through electron spin-lattice relaxation, the process is repeated again and again, until all the nuclear spin polarisation is lost.

There are traditionally two approaches to treat direct nuclear spin-lattice relaxation, both leading to the same result. In his original, *random field* approach, Bloembergen considered the electron spins to be fluctuating between the up and down state due to their interaction with the lattice. This results in a fluctuating magnetic field at the position of the nuclear spins and the component of this fluctuating field at the frequency ω_{0I} induces transitions of the nuclear spins [16, 17]. This approach is semi-classical, because the fluctuating field is considered a classical field.

In the *scrambled state* approach one proceeds in the same way as for the solid effect. Again one considers the electron spin states and the nuclear spin states to be mixed by the super-hyperfine interaction. The electron spin-lattice interaction induces transitions between these mixed states, thus causing the electron spins and the nuclear spins to flip simultaneously. Leifson and Jeffries used this method to describe both the solid effect and nuclear spin-lattice relaxation [9]. This approach is fully quantum mechanical, but, as nicely demonstrated by Abragam and Goldman, it is completely equivalent to the random field approach [18].

4. Thermal Mixing

A simple picture of the processes playing a role in DNP via thermal mixing is presented in Figure 2a. Similar to Figure 1a the large arrows represent the polarisation of several electron spins S, S', etc., and the small arrows the polarisation of some nuclear spins I, I', etc., surrounding S. The top row shows the initial conditions. As in our description of the solid effect we start with a high electron spin polarisation, and a low nuclear spin polarisation. So, as in Figure 1a all large arrows are up and the orientation of the small arrows is random. Again our aim is to render all small arrows up. But to achieve this aim, we now tune the microwave frequency to the resonance frequency ω_S of the electron spin S''. As a result this electron spin flips and we arrive at the situation depicted in the second row.

The mutual interaction between the electron spins induces flip-flop transitions and the reversal of the polarisation of S'' is rapidly transferred to another spin, e.g., S'. But once in a while, the mutual interaction $\mathbf{S}' \cdot \mathbf{D} \cdot \mathbf{S}$ between, e.g., S' and S combines with the super-hyperfine interaction $\mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}$ and induces a *triple spin flip* of the two electron spins and a nearby nuclear spin I. The rate of such triple spin flips is much smaller than the rate of simple flip-flop transitions. So many

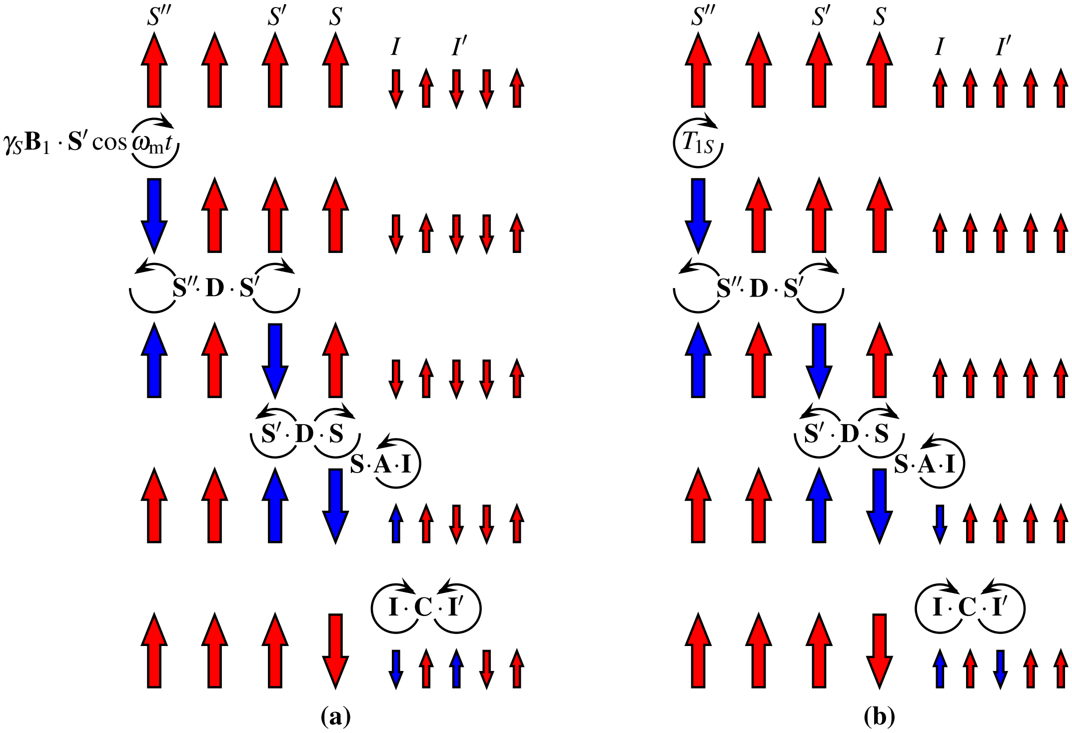

Figure 2: (a) Cartoon depicting the fundamental processes involved in DNP via thermal mixing. (b) Cartoon depicting the fundamental processes involved in nuclear spin-lattice relaxation via thermal mixing. For the explanation see the text.

simple flip-flop transitions may occur before a triple spin flip takes place. The third row shows how triple spin flips transfer the polarisation of S to a nearby nuclear spin, while S' recovers its original orientation.

Subsequently, just as in the solid effect the resulting nuclear spin polarisation is transported to the nuclear spins further away by the mutual interaction $\mathbf{I} \cdot \mathbf{C} \cdot \mathbf{I}'$ between the nuclear spins. Furthermore, the electron spin S flips back via electron spin-lattice relaxation or a flip-flop transition with another electron spin. This allows the process to start all over again, so more nuclear spins are polarised. But this last step is omitted from the figure.

Triple spin flips as shown in Figure 2a not only serve to increase the nuclear polarisation when a microwave field is applied. They also contribute to nuclear spin-lattice relaxation in a mechanism, which we will call *indirect nuclear spin-lattice relaxation*. Figure 2b illustrates how. As in the previous figures the large arrows represent the polarisation of several electron spins S, S', etc., and the small arrows the polarisation of some nuclear spins I, I', etc., surrounding S. Again the top row shows the initial conditions, and, as for direct nuclear spin-lattice relaxation we assume that we have successfully polarised the nuclear spins, so all small arrows point up.

The sample cannot be cooled to absolute zero and electron spin-lattice relaxation flips the electron spins between up and down with a rate T_{1S}^{-1}. In Figure 2b this is shown for the electron spin S''. The mutual interaction between the electron spins induces flip-flop transitions and the reversal of the polarisation of S'' is rapidly transferred to another spin, e.g., S'. But as in Figure 2b every now and then the mutual interaction $\mathbf{S}' \cdot \mathbf{D} \cdot \mathbf{S}$ between e.g., S' and S combines with the super-hyperfine interaction $\mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}$, and induces a triple spin flip of the two electron spins and a nuclear spin I. The third row shows how such a triple spin flip transfers the polarisation of a nearby nuclear spin I back to S, while S' recovers its original orientation. Subsequently, nuclear spin diffusion transfers this loss of polarisation to the nuclear spins further away. Not shown is how the electron spin S finally flips back via electron spin-lattice relaxation or flip-flop transitions with other electron spins, which allows the process to start all over again until all nuclear spin polarisation is lost.

The understanding and the acceptance of thermal mixing as a mechanism for DNP have a long history. Those interested will find an informative overview in [19]. It all starts in 1963, when Kessenikh proposes the triple spin transition and describes it on the basis of a *scrambled state* approach [20]. So he considers the electron spin states and the nuclear spin states to be mixed by the super-hyperfine interaction and the mutual interaction between the electron spins to induce transitions between these mixed states. This work was later taken up by several authors [21, 22, 23, 24] and described this way, the mechanism of DNP via triple spin transitions became eventually known as the *cross effect*.

Independently Kozhushner and Provotorov proposed this fundamental transition in a meeting in 1964 and described it on the basis of a *fluctuating field* approach [25]. So they considered the electron spins to be fluctuating between the up and down state due to their mutual interaction and the component of this fluctuating field at the NMR frequency to induce transitions of the nuclear spins. Unfortunately, the proceedings did not appear before 1967 and were never translated from Russian. Moreover Kozhushner waited until 1969 to publish their proposal in a journal which was regularly translated into English [26]. But already in 1965 Buishvili had picked up the idea and published a theoretical paper, in which he treats DNP and nuclear spin-lattice relaxation via the mechanism proposed by Kozhushner and Provotorov [27]. Described this way, the mechanism of DNP via triple spin transitions became known as *thermal mixing*.

Early treatments of the cross effect in e.g. [21, 22] do not account for spectral diffusion in the ESR line. Already in 1969 Borghini and Scheffler [28] realised that spectral diffusion needs to be added to these early treatments. There are two reasons to add spectral diffusion. First, triple spin flips need not only the super-hyperfine interaction between electron spins and nuclear spins, but also the mutual interaction between electron spins. Triple spin flips are second order transitions and occur at a much slower rate than the first order flip-flop transitions between electron spins induced by just the mutual interaction between electron spins. But the latter flip-flop transitions also cause spectral diffusion across the ESR spectrum. Hence, if triple spin flips occur, there is also spectral diffusion.

The second reason is even more compelling. If spectral diffusion is weak and the microwave field only burns a hole in the ESR signal, the number of electron spins available for transfer of polarisation to the nuclear spins is equal to the number of electron spins in the hole. Electron spins outside the hole don't participate in the process depicted in Figure 2a. On the other hand, *all* electron spins participate in the relaxation process depicted in Figure 2b. Only few triple spin flips contribute to the growth of the nuclear spin polarisation, while many — equally probable — triple spin flips contribute to the decay of the nuclear spin polarisation. Hence, unless spectral diffusion is fast, triple spin flips don't contribute significantly to the polarisation transfer in DNP.

A treatment of triple spin flips shows that thermal mixing and the cross effect are identical mechanisms, when fast spectral diffusion is included. There is just one exception. The rate of triple spins can be strongly enhanced, either using paramagnetic centres with electron spin $S > \frac{1}{2}$

[29, 30] or embedding two electron spins in a single radical [31]. Then the ESR spectrum consists of more than one ESR line, and fast spectral diffusion over the whole ESR spectrum may not be needed, if the splitting between two lines is equal to the NMR frequency. To avoid confusion, the name *cross effect* is to be preferred for this special situation, and the term *thermal mixing* for all other manifestations of this mechanism of DNP.

A significant body of experimental work, notably in Moscow and Leiden — for reviews of this work see [32] and [33] — supported the existence of thermal mixing as a mechanism for DNP and nuclear spin-lattice relaxation, but some people remained sceptical. Even Abragam had reservations, even though already in 1963 his group observed a similar mechanism inducing the transfer of polarisation from one type of nuclear spin to another [34]. This lasted until 1973, when Cox, Bouffard and Goldman succeeded to measure the rate of triple spin transitions in LiF doped with F-centres [35, 36], and to explain the result with the fluctuating field approach. At the same time Goldman observed that the cross effect and thermal mixing are actually the same process: the fluctuating field approach and the scrambled state approach should lead to the same rate for the polarisation transfer [37]. Henceforward, both the solid effect and thermal mixing were accepted to contribute to DNP, in some cases the former dominating the polarisation transfer, in other cases the latter. Soon even examples appeared where both mechanisms are active at the same time [38].

5. Final Remark

After more than half a century of research, the theory of DNP is still incomplete. The most important missing element is an extension of Provotorov's theory to general temperatures. A partial extension exists, in which the electron Zeeman reservoir is treated for general temperatures, and the electron non-Zeeman reservoir in the high temperature approximation [39]. But, as soon as a microwave field is applied, and the two reservoirs are coupled, this existing extension becomes tricky. Hopefully, the present revival of DNP incites theorists to tackle such problems.

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