Addendum A: The Cross Effect

This addendum provides additional material to Sections 8.3.1 and 8.3.4 of Essentials of Dynamic Nuclear Polarization, Spindrift Publications, 2016—to be denoted henceforward shortly as *EofDNP*. It extends the notion of the cross effect to all enhancement of the nuclear spin polarization by triple spin flips in the case that the microwave field burns a hole in the ESR signal.

1. Introduction

Early treatments of the cross effect in e.g. [7, 8] do not account for spectral diffusion in the ESR line. Already in 1969 Borghini and Scheffler [4] realized that spectral diffusion needs to be added to these early treatments. There are at least 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. The triple spin flips leading to the cross effect 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 electrons. 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. In the absence of spectral diffusion the microwave field just burns a narrow hole in the ESR signal. But only triple spin flips involving one electron spin with its resonance frequency in the hole transfer polarization to the nuclear spins. Triple spin flips involving *all* other pairs of electron spins lead to the nuclear spin-lattice relaxation. So, only few triple spin flips contribute to the growth of the nuclear spin polarization, while many—equally probable—triple spin flips contribute to the decay of the nuclear spin polarization. Hence, spectral diffusion is needed for triple spin flips to contribute significantly to the polarization transfer in DNP.

For triple spin flips to lead to an appreciable enhancement of the nuclear spin polarization, spectral diffusion needs to be sufficiently fast, so the hole burnt by the microwave field is wide. But, as we will see below, the solid effect still dominates the polarization process, provided sufficient microwave power is applied. Only when spectral diffusion is so fast, that the full ESR signal is saturated and its shape has to be described by Provotorov's theory, triple spin flips always dominate DNP. Then the cross effect introduced by Kessenich and thermal mixing proposed by Kozhushner are identical mechanism. To avoid confusion, we reserve the name *cross effect* for DNP via triple spin flips, when a hole can be burnt in the ESR signal, and the term *thermal mixing* for DNP via triple spin flips, when the saturation of the ESR signal has to be described by Provotorov's theory.

2. Transition from the Solid Effect to Thermal Mixing: the Cross Effect

When condition (8.92) in *EofDNP* holds, the microwave field burns a hole in the ESR signal, but the rate of triple spin flips is faster than the rate of direct nuclear spin-lattice relaxation. This enables us to ignore direct nuclear spin-lattice relaxation

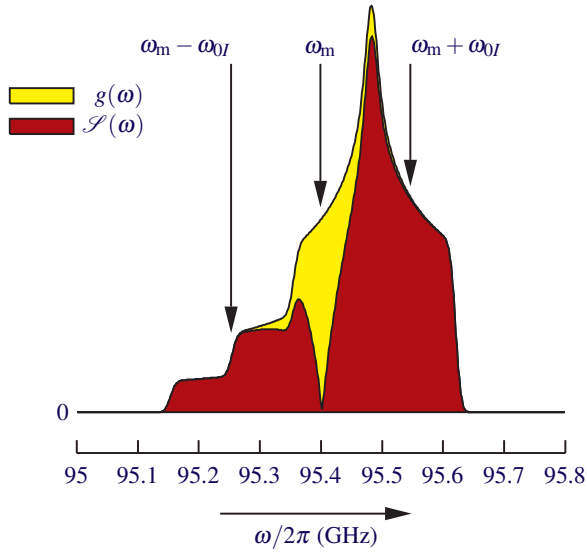

Figure 1: Simulation of the ESR signal resulting from to the simultaneous action of the microwave field, spectral diffusion and electron spin-lattice relaxation, as shown in Figure 5.10 of *EofDNP*. For the details, see the caption of that figure. Triple spin flips involving electron spins with a resonance frequency near ω_m and $\omega_m \pm \omega_{0I}$ contribute to enhancement of the nuclear spin polarization. All other triple spin flips contribute to nuclear spin-lattice relaxation.

in what follows. To investigate the effect of triple spin flips on the evolution of the nuclear spin polarization P_I, we return to the rate equation (8.54) in *EofDNP*:

$$\frac{\partial P_I}{\partial t} = -\tfrac{1}{2}\pi \frac{N_S}{N_I} \frac{A^2 M_2^0}{\omega_{0I}^2} \int_{-\infty}^{\infty} \mathrm{d}\omega \; g(\omega)\, g(\omega - \omega_{0I}) \times \left[1 - P_S(\omega) P_S(\omega - \omega_{0I})\right] \left[P_I - \frac{P_S(\omega) - P_S(\omega - \omega_{0I})}{1 - P_S(\omega) P_S(\omega - \omega_{0I})}\right]. \qquad (1)$$

It describes the evolution of P_I that results from triple spin flips involving pairs of electron spins with resonance frequencies ω and $\omega - \omega_{0I}$. If, as illustrated for TEMPO in Figure 1, a hole is burnt in the ESR signal, the polarization of the majority of such pairs of electron spins is equal to P_L. These pairs let the nuclear spin polarization decay to zero. But if the resonance frequency of one of the two electron spins is in the hole burnt by the microwave field, $P_S(\omega)$ differs strongly from $P_S(\omega - \omega_I)$. Such pairs contribute to enhancement of the nuclear spin polarization P_I. But, as pointed out by Borghini and Scheffler [4], if the hole is narrow, only few triple spin flips contribute to the growth of the nuclear spin polarization, while many more—equally probable—triple spin flips contribute to the decay of the nuclear spin polarization. So the enhancement due to triple spin flips is small.

To quantify their statement, we start with (1) and introduce some simplifying approximations. First, we assume that $P_S(\omega) \leq P_L \ll 1$. This approximation is not

unreasonable: Section 5.3.1 of *EofDNP* demonstrates that the electron spin-lattice relaxation time generally needs to be fairly short—$T_{1S} \ll 1$ ms—in order to be able to burn a hole in ESR signal. To shorten the electron spin-lattice relaxation time to such low values, one often needs to raise the temperature to above 4 K, where $P_{\rm L} \ll 1$. Secondly, we assume that the hole is narrower than the NMR frequency ω_{0I}. Then $P_S(\omega) = P_S(\omega - \omega_{0I}) = P_{\rm L}$, except when either ω is near the microwave frequency $\omega_{\rm m}$, so $\omega - \omega_{0I} \approx \omega_{\rm m} - \omega_{0I}$, or when $\omega - \omega_{0I}$ is near the microwave frequency $\omega_{\rm m}$, so $\omega \approx \omega_{\rm m} + \omega_{0I}$. These two approximations enable us to rewrite (1) in the shape

$$\frac{\partial P_I}{\partial t} \;=\; -\tfrac{1}{2}\pi\,\frac{N_S}{N_I}\,\frac{A^2 M_2^0}{\omega_{0I}^2}\Bigg\{ g(\omega_{\rm m}-\omega_{0I})\int_{-\infty}^{\infty}\mathrm{d}\omega\; g(\omega)\,\big[P_I - P_S(\omega) + P_{\rm L}\big] \\ + g(\omega_{\rm m}+\omega_{0I})\int_{-\infty}^{\infty}\mathrm{d}\omega\; g(\omega)\,\big[P_I - P_{\rm L} + P_S(\omega)\big]\Bigg\}\,. \tag{2}$$

In this expression the ESR line shape $g(\omega)$ is normalized:

$$\int_{-\infty}^{\infty}\mathrm{d}\omega\; g(\omega) \;=\; 1\,. \tag{3}$$

We furthermore define the average electron spin polarization

$$\overline{P_S} \;=\; \int_{-\infty}^{\infty}\mathrm{d}\omega\; g(\omega)\,P_S(\omega) \;=\; (1-r)P_{\rm L}\,. \tag{4}$$

Here $1-r$ is the reduction of the average electron spin polarization with respect to its thermal equilibrium value $P_{\rm L}$. We refer to Figure 1 to illustrate this quantity. It corresponds to the ratio of the red area and the area of the full line shape. Hence, r corresponds to the ratio the yellow area and the area of the full line shape. We finally complete the picture adding the solid effect as in (8.90) and (8.91) of *EofDNP*:

$$\frac{\partial P_I}{\partial t} \;=\; -\,\pi\,\frac{N_S}{N_I}\,\frac{A^2}{\omega_{0I}^2}\Big\{ \omega_{1S}^2 g(\omega_{\rm m}+\omega_{0I})\big[P_I - P_{\rm L}\big] + \omega_{1S}^2 g(\omega_{\rm m}-\omega_{0I})\big[P_I + P_{\rm L}\big] \\ + \tfrac{1}{2}M_2^0 g(\omega_{\rm m}+\omega_{0I})\big[P_I - rP_{\rm L}\big] + \tfrac{1}{2}M_2^0 g(\omega_{\rm m}-\omega_{0I})\big[P_I + rP_{\rm L}\big]\Big\}. \tag{5}$$

Let us discuss this result. If $\omega_{1S}^2 \ll \frac{1}{2}M_2^0$, triple spin flips dominate the evolution of the nuclear spin polarization P_I. This leads to an enhancement of the nuclear spin polarization, albeit reduced by a factor r compared to what can be obtained with the differential solid effect and—as we will see below—with thermal mixing. We follow the convention mentioned above, and, when a hole can be burnt in the ESR signal, we denote the mechanism of DNP by triple spin flips as the *cross effect*. Recent studies of the cross effect and its relation to the solid effect are presented in [6, 9].

There are two strategies to increase the nuclear spin polarization that can be reached in this regime. In the first strategy one simply increases the microwave power, such that $\omega_{1S}^2 \gg \frac{1}{2}M_2^0$. Then the nuclear spins are polarized by the solid effect, while they relax via triple spin flips. In the second strategy one searches to lengthen the

electron spin-lattice relaxation time, for example by lowering the temperature. According to the treatment of hole burning in Section 5.3.1 in *EofDNP*, the hole then widens, so r increases. Eventually, the hole covers the full ESR spectrum, and we need to describe the saturation of the ESR signal using Provotorov's theory. This is the regime of thermal mixing discussed in Sections 8.3.2 and following of *EofDNP*.

When the width of the hole approaches the width of the ESR spectrum, but Provotorov's theory cannot yet be applied, the cross effect becomes already efficient. Unfortunately, the treatment of spectral diffusion in Sections 4.2.1 to 4.2.4 in *EofDNP* is not sufficiently sophisticated to calculate the shape of such wide holes. This theoretical problem can be avoided, if the ESR spectrum is split into several narrow lines.

3. Composite ESR Spectra

Except for Section 8.3.4, Chapter 8 of *EofDNP* considers ESR spectra consisting of a single resonance line. Here we present an extension Section 8.3.4 and review the various regimes of DNP for composite ESR spectra consisting of several ESR lines. Splitting of the ESR spectrum may be observed in single crystals, when there are two or more non-equivalent sites for paramagnetic centres. Also fine splitting or hyperfine interaction may then split the ESR spectrum. The origin of such splittings is, however, not relevant for our discussion.

As we will see below, composite ESR spectra played a prominent part in some early studies of thermal mixing. Such composite spectra are also useful for a better understanding of the cross effect. As explained above, in the transitional regime between the solid effect and thermal mixing the microwave field still burns a hole in the ESR signal and a single electron non-Zeeman temperature is not yet established. But triple spin flips may already enhance the nuclear spin polarization: the cross effect. We noted that the cross effect becomes efficient when the width of the hole burnt by the microwave field becomes comparable to the width of the ESR spectrum. But we also noted that our treatment of spectral diffusion in Sections 4.2.1 to 4.2.4 of *EofDNP* is not sufficiently sophisticated to calculate the shape of such wide holes. We can circumvent this problem considering composite ESR spectra.

Figure 2 shows the ESR signal for a spectrum consisting of two well separated lines, I and II, each narrow compared to the NMR frequency ω_{0I}. We assume the extreme case that electron spin-lattice relaxation is fast compared to spectral diffusion, so the microwave field burns a hole in one of the resonance lines, just as shown Figure 1. When the electron spin-lattices relaxation rate is so fast that also condition (8.88) in *EofDNP* holds, DNP is dominated by the solid effect and the nuclei relax via direct nuclear spin-lattice relaxation.

Figure 3 shows the ESR signal for the same spectrum, but now for the other extreme case, in which electron spin-lattice relaxation is so slow, that spectral diffusion can spread the saturation across the full ESR spectrum. In this case the treatment presented in the previous two sections remains valid, and nuclear spins are polarized by thermal mixing.

Atsarkin, Mefed and Rodak reported a thorough investigation of thermal mixing in this regime on single crystals of ruby (Al_2O_3) doped with Cr^{3+}-ions [1, 2, 3]. In these samples, fine splitting separates the ESR spectrum of the electron spin $S = \frac{3}{2}$ of the

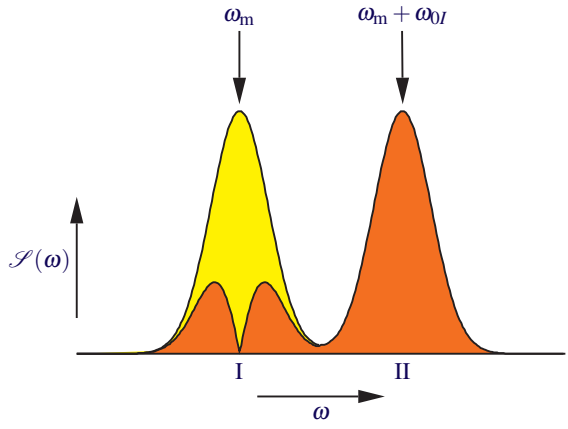

Figure 2: ESR signal displaying two separated ESR lines I and II. A hole is burnt at the microwave frequency ω_m. Triple spin flips at the frequencies ω_m and $\omega_m \pm \omega_{0I}$ contribute to enhancement of the nuclear spin polarization. All other triple spin flips contribute to nuclear spin-lattice relaxation.

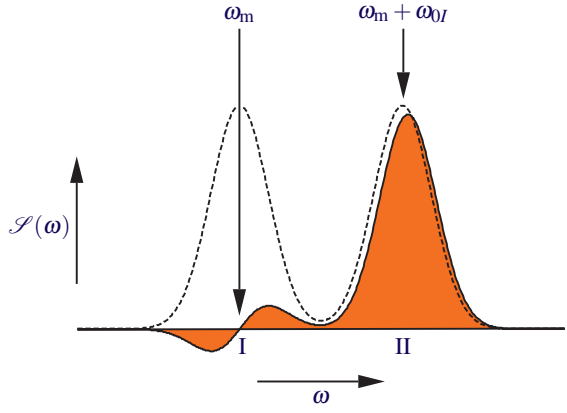

Figure 3: ESR spectrum consisting of two separated ESR lines I and II. Spectral diffusion is fast compared to electron spin-lattice relaxation, and Provotorov's theory describes the saturation of the ESR signal. Triple spin flips tend to equalize the inverse electron non-Zeeman temperature and the inverse nuclear spin temperature.

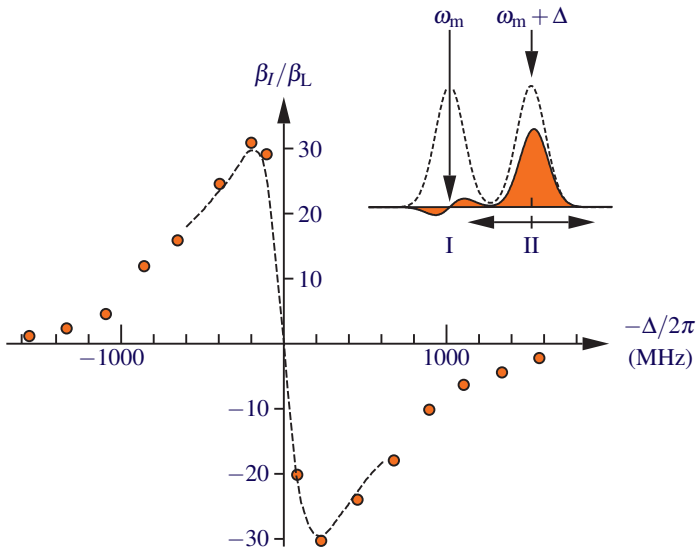

Figure 4: Observation of thermal mixing by Atsarkin, Mefed and Rodak in single crystals of ruby (Al_2O_3) doped with Cr^{3+}-ions. For a detailed explanation see the text. Figure redrawn from [2, 3].

Cr^{3+}-ions into three resonance lines, which we will denote here as the $m_S = -\frac{3}{2} \leftrightarrow -\frac{1}{2}$ (II), the $m_S = -\frac{1}{2} \leftrightarrow +\frac{1}{2}$ (I) and the $m_S = +\frac{1}{2} \leftrightarrow +\frac{3}{2}$ (III) transition. The separation between these resonance lines can be varied by changing the orientation of the static magnetic field with respect to the crystal axes.

Figure 4 presents some results of experiments on a sample containing 0.03% Cr^{3+}-ions. At liquid helium temperature a microwave field with a frequency $\omega_m/2\pi = 9.3$ GHz was tuned to the centre of the I transition. By rotating the sample, the frequency of the II transition was varied in the range $8.7 \leq (\omega_m + \Delta)/2\pi \leq 10.9$ GHz. For each value of Δ the inverse nuclear spin temperature β_I was measured after a long time of microwave irradiation. Figure 4 shows β_I/β_L as a function of $\Delta/2\pi$. The shape of the ESR signal was also monitored. From this shape it was inferred that the electron spin system could be described by a single electron non-Zeeman temperature. Moreover, this temperature was found to be equal to the nuclear spin temperature, thus confirming fast thermal mixing.

Similar results were obtained for the polarization transfer from the electron spin $S = \frac{1}{2}$ of Cu^{2+} to the proton spins $I = \frac{1}{2}$ in the Tutton salts $ZnX_2(S0_4)_2.6H_20$ (X = NH_3, K, Rb, Cs), where the ESR spectrum is split into four equidistant resonance lines separated by 230 MHz [10, 11]. However, the description needed to be modified for stronger microwave fields that induce electron spin flips at a faster rate than spectral diffusion can spread the saturation across the full ESR spectrum [5].

We now turn our attention to the intermediate case, in which the condition (8.92) in *EofDNP* holds. Then direct nuclear spin-lattice relaxation can be ignored, and we only need to account for triple spin flips and the solid effect. The microwave field still burns a hole in the ESR signal as shown in Figure 2. Triple spin flips involving pairs of electron spins with a resonance frequency near $\omega_{\rm m}$ and $\omega_{\rm m} \pm \omega_{0I}$ contribute to enhancement of the nuclear spin polarization. All other triple spin flips contribute to nuclear spin-lattice relaxation. The net result is some enhancement of the nuclear spin polarization via the cross effect. But, as argued above, if we apply sufficient microwave power, the solid effect yields a significantly higher polarization, and then dominates DNP.

However, when the electron spin-lattice relaxation rate slows further, the hole widens and the enhancement of the nuclear spin polarization by the cross effect increases. Eventually, one of the two resonance lines is completely saturated. We describe this case, assuming that spectral diffusion is fast within each individual ESR line, but slow across the full ESR spectrum. This may occur when the individual ESR lines are sufficiently separated. Then flip-flop transitions involving electron spins with their resonance frequencies in different resonance lines are slowed down. This follows from the flip-flop transition rate (4.28) in *EofDNP*, in which the convolution (4.26) then becomes very small or may even vanish. However, triple spin flips are still possible, because they involve electron spins with resonance frequencies separated by the NMR frequency ω_{0I}. Now, before continuing, notice the following. As we saw in Section 8.2.2 of *EofDNP*, triple spin flips also tend to establish a single non-Zeeman temperature. Hence, if the electron spin-lattice relaxation rate is sufficiently slow, such a single non-Zeeman temperature will still be established. We do not need fast spectral diffusion across the full ESR spectrum.

To investigate this intermediate case we assume that a microwave field saturates one of the two resonance lines and determine the evolution of the nuclear spin polarization due to triple spin flips. We start with the general expression (8.54) in *EofDNP* for the evolution of the nuclear spin polarization due to triple spin flips:

$$\begin{aligned}\frac{\partial P_I}{\partial t} \;=\; & -\tfrac{1}{2}\pi\,\frac{N_S}{N_I}\,\frac{A^2 M_2^0}{\omega_{0I}^2}\int_{-\infty}^{\infty} \mathrm{d}\omega\; g(\omega)\; g(\omega-\omega_{0I}) \\ & \times\big[1-P_S(\omega)P_S(\omega-\omega_{0I})\big]\left[P_I-\frac{P_S(\omega)-P_S(\omega-\omega_{0I})}{1-P_S(\omega)P_S(\omega-\omega_{0I})}\right]. \qquad (6)\end{aligned}$$

The spectral density $g(\omega)$ in the integral on the right hand side represents the full ESR spectrum. We split this function into two parts

$$g(\omega) \;=\; g_{\rm I}(\omega) \;+\; g_{\rm II}(\omega)\,, \qquad (7)$$

where $g_{\rm I}(\omega)$ and $g_{\rm II}(\omega)$ are the shapes of the two individual resonance lines. The two resonance lines do not overlap, and their width is much less than the NMR frequency ω_{0I}. So

$$\begin{aligned} g(\omega)\,g(\omega-\omega_{0I}) \;=\; & g_{\rm I}(\omega)\,g_{\rm I}(\omega-\omega_{0I}) \;+\; g_{\rm I}(\omega)\,g_{\rm II}(\omega-\omega_{0I}) \\ & +\, g_{\rm II}(\omega)\,g_{\rm I}(\omega-\omega_{0I}) \;+\; g_{\rm II}(\omega)\,g_{\rm II}(\omega-\omega_{0I}) \\ \;=\; & g_{\rm I}(\omega)\,g_{\rm II}(\omega-\omega_{0I})\,. \qquad (8)\end{aligned}$$

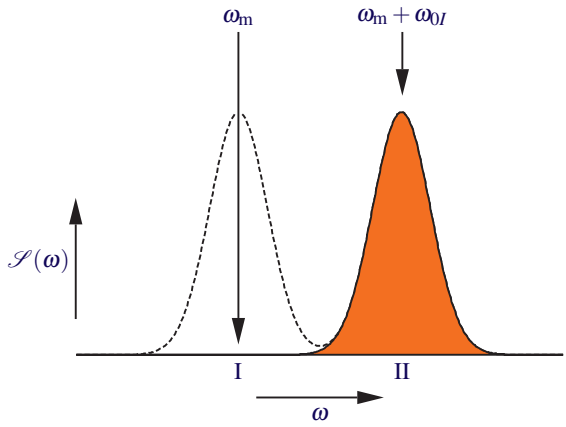

Figure 5: ESR spectrum consisting of two separated ESR lines I and II. Spectral diffusion is fast within each individual ESR line, but slow across the full ESR spectrum. When the separation of the two ESR lines is near the NMR frequency ω_{0I}, the cross effect governs the enhancement of the nuclear spin polarization in DNP and nuclear spin-lattice relaxation.

This function is non-zero only for ω in the low frequency ESR line and $\omega-\omega_{0I}$ in the high frequency ESR line. But then $P_S(\omega)$ only concerns electrons spins with their resonance frequency in the low frequency ESR line, and $P_S(\omega-\omega_{0I})$ only concerns electrons spins with their resonance frequency in high frequency ESR line.

We now investigate what happens, when we apply a strong microwave field with its frequency at the centre of the low frequency resonance line. Spectral diffusion is fast across that resonance line. The Provotorov equations then yield $P_S(\omega)=0$. But spectral diffusion across the full ESR spectrum is too slow to transfer saturation to the other resonance line. So $P_S(\omega-\omega_{0I})$ remains at its equilibrium value $P_{\rm L}$ with the lattice. As a result the ESR signal acquires the shape shown in Figure 5. Then the rate equation (6) for the evolution of the nuclear spin polarization reduces to

$$\frac{\partial P_I}{\partial t} \;=\; -\,\frac{1}{\tau_{\rm pol}}\,(P_I-P_{\rm L})\;, \tag{9}$$

in which

$$\frac{1}{\tau_{\rm pol}} \;=\; \tfrac{1}{2}\pi\,\frac{N_S}{N_I}\,\frac{A^2M_2^0}{\omega_{0I}^2}\int_{-\infty}^{\infty}{\rm d}\omega\; g_{\rm I}(\omega)\; g_{\rm II}(\omega-\omega_{0I}) \tag{10}$$

is the polarization rate. The convolution on the right hand side peaks when the distance between the two resonance lines is equal to the NMR frequency ω_{0I}. Then the nuclear spin polarization P_I grows rapidly towards the stationary value $P_{\rm L}$, just as high as with the solid effect. When the distance between the two lines is somewhat smaller or larger than ω_{0I}, the nuclear spin polarization P_I still grows, but at a lower rate. But when the distance between the resonance lines becomes too large, the convolution vanishes, and no enhancement of P_I is obtained.

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