Dynamic nuclear polarization: Yesterday, today, and tomorrow

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Abstract. A review is given of the history and basic principles of dynamic nuclear polarization (DNP) in condensed matter, starting from the Overhauser pioneering work and up to the modern applications in chemistry and medicine. Different physical mechanisms of DNP, such as the Overhauser effect, solid effect, electron-nuclear cross relaxation, and thermal mixing are considered. Further prospects of the DNP techniques for future are discussed.

Dynamic nuclear polarization (DNP) consists in transferring high spin polarization from the electrons of paramagnetic impurities to the host nuclei by means of microwave irradiation close to EPR frequency. This technique, firstly suggested for condensed matter by A. Overhauser in 1953 [1], became a powerful method of modern science, being applicable to a wide variety of urgent problems such as polarized targets for particle physics, giant increase in NMR sensitivity, spin thermodynamics in solids, etc. Keeping in mind the memorial type of this Conference dedicated to the Centenary of Professor S. A. Altshuler, this report is focused primarily on historical aspects, beginning from the Overhauser’s discovery and up to contemporary “new Renaissance”. Main attention will be paid to various physical mechanisms of DNP, and especially to the role playing by spin-spin interactions. Some traditional and novel applications will be touched as well.

The restricted volume of this article dictates laconic style. In fact, we do not pretend to any exhaustive review with a vast list of references. Instead, a conceptual sketch is proposed, including the main milestones only, with citing preferably to books, review articles, and the most principal papers.

Let us start with definitions. Consider a solid sample containing host nuclei with nuclear spins I and paramagnetic impurities with electron spins S. Spin polarization $P_{I,S} = \langle \hat{I}^z, \hat{S}^z \rangle / (I, S)$ is defined as a fraction of spins (nuclear or electronic) directed along the external magnetic field $H_{ex}$ for spins $1/2$, the polarization values at the equilibrium temperature $T_0$ are

$$P_{I,S}^0 = \tanh \left( \frac{\hbar \gamma_{I,S} H}{2k_B T_0} \right)$$

where $\gamma_{I,S}$ are the nuclear and electronic magnetogyratic ratios, respectively, and common notations for Planck and Boltzmann constants are used. One can see that, even at high magnetic field of 5 T and very low temperature $T_0 = 0.5$ K, the equilibrium polarization of protons is merely about 0.01, whereas $P_{S}^0 \approx -1$.

As mentioned above, the DNP techniques enables one to transfer high polarization from electrons to nuclei. To do this, Albert Overhauser suggested [1] to saturate the EPR line with resonant
microwaves and employ specific relaxation processes with simultaneous flips of electronic and nuclear spins in opposite directions. Such relaxation can be governed by the scalar (contact) hyperfine interaction of the \( A(I\cdot S) \) type. To compensate the energy mismatch, the correlation function should have considerable spectral density \( J(\omega_S + \omega_I) \sim J(\omega_S) \), where \( \omega_S = -\gamma_S H \) and \( \omega_I = \gamma_I H \) are, respectively, the EPR and NMR frequencies. Since the \( \omega_S \) value is commonly high enough, the Overhauser Effect (OE) is characteristic for systems with fast motion of electron spins, such as metals and materials with strong S-S exchange. The enhancement of nuclear polarization, \( E = P/I^0 \), was predicted to amount \( \omega_S/\omega_I \) (at maximum), that is about 660 for protons.

The Overhauser’s idea was soon confirmed by T. P. Carver and C. P. Slichter who performed DNP experiments on Li metal [2]. A bit later, A. Abragam suggested another version of this effect employing dipole-dipole electron-nuclear interactions [3]. This kind of OE works in liquids and provides the maximum enhancement of \(-\omega_S/2\omega_I\). The Overhauser mechanism of DNP was also applied successfully to the nucleus-nucleus spin-spin interaction; this version, known as Nuclear Overhauser Effect (NOE), is widely used in the NMR spectroscopy [4].

The next step in the DNP history is related to the work by Abragam and Proctor published in 1958 [5] (see also the famous Abragam’s book [6]). Instead of employing specific electron-nuclear relaxation, they proposed to use the electron-nuclear transitions induced by microwave pumping at the frequencies \( \omega_S \pm \omega_I \). Formally, these “satellite” transitions are forbidden, but become slightly allowed due to the dipole-dipole interactions between paramagnetic center and neighboring nuclei, owing to the operators like \( \hat{I}^z \hat{S}^z \). The authors [5] named this mechanism “Solid Effect” (SE) because of its applicability mostly to non-conducting solids. The maximum enhancement of nuclear polarization due to SE amounts to \( \pm \omega_S/2\omega_I \), the sign being dependent on the hyperfine satellite chosen for saturation. An essential condition for successful SE experiment is nuclear spin diffusion [7] which provides the spreading of enhanced polarization from the nearest neighbors of paramagnetic centers throughout the sample volume. Besides, the electron spin-lattice relaxation time \( T_{1S} \) should be short enough (much less than the nuclear one, \( T_{1I} \)), in order to provide numerous electron-nuclear flips via every paramagnetic center.

The SE is most effective when the EPR line-width \( \delta_S \) is much less than \( \omega_I \), so the “forbidden” satellites are well resolved. A sketch of typical \( E(\omega_S) \) dependence for such a case is shown in figure 1.

![Figure 1](image-url)
Numerous results of this type were obtained on various single crystals, such as \( \text{La}_2\text{Mg}_3(\text{NO}_3)_{12}\cdot24\text{H}_2\text{O} \) (LMN) doped with \( \text{Nd}^{3+} \) [8] and others, where the EPR line was sufficiently narrow. The SE was thoroughly studied worldwide and successfully applied in building the first high-polarized proton targets working at liquid helium temperatures in magnetic fields up to 2.5 T. An excellent description of the DNP physics and applications as of the early 60-s was presented by C. D. Jeffries; his monograph [9] became a handbook for the DNP community.

At this stage, however, some difficulties arose. To provide high enough concentration of protons in a polarized target, it was necessary to turn from single crystals, such as LMN, to some frozen alcohols, like glycerol, ethylene glycole, etc. The EPR lines of stable radicals or paramagnetic ions in such systems are inhomogeneously broadened due to the anisotropy of g-factor. The electron dipole-dipole interactions between paramagnetic centers also contributes to the EPR line width and, in any case, leads to effective spectral diffusion (electron spin-spin cross relaxation) throughout the line. As a result, the “forbidden” satellites overlap with each other and with the central (allowed) EPR transition, and cannot be saturated separately. At the first glance, this should strongly diminish or even cancel the DNP effect.

As is often the case, the solution was found owing to the same factor which created the problem, namely, the spin-spin interaction. In 1963, A. V. Kessenikh and A. A. Manenkov suggested the 3-spin Cross Effect (CE) [10], involving simultaneous flips of two electronic and one nuclear spins, see figure 2. Such a process is caused by the dipole-dipole operators like \( \hat{S}_a^z \hat{S}_b^z I^z \) and requires the energy matching,

\[
\omega_S^a - \omega_S^b = \omega_I
\]  

so the paramagnetic species \( a \) and \( b \) should have different g-factors. It should be emphasized that, in contrast to the Solid Effect, now it is sufficient to saturate an allowed (not forbidden) transition corresponding to one or another electron spin species, the resulting nuclear polarization being equal to \( P_a \). In particular, equation (2) can be applied to two spin packets separated by the \( \omega_I \) distance inside the inhomogeneously broadened EPR line with the width \( \delta_S^\text{inh} > \omega_I \). In this case, the 3-spin Cross Effect becomes much more effective than SE.

![Figure 2](image_url)  

**Figure 2.** An elementary act of the 3-spin electron-nuclear cross relaxation.

Some experimental evidences for the 3-spin CE, as well as more detailed theoretical discussion were published by various authors [11]. However, this was the first step only. Evidently, a lot of spin packets in the inhomogeneous EPR line do not satisfy the condition (2). To take into account all spin-spin processes, including the ordinary electron spin-spin cross relaxation, a strict many-particle theory was needed, based on quantum statistics and spin thermodynamics.

Such theory was advanced by B. N. Provotorov in 1961 [12]. According to the Provotorov’s equations, saturation of magnetic resonance with some detuning from the central frequency results in strong cooling of the quasi-equilibrium subsystem formed by the secular part of the spin-spin (mostly, dipole-dipole) interactions. This so-called spin-spin reservoir has a quasi-continuous spectrum in the range of the mean local (dipolar) frequency and can be characterized by its own temperature which, generally, differs from the ordinary Zeeman spin temperature and can be either positive or negative,
depending of the saturation detuning. In real samples, the NMR frequency $\omega_I$ often falls into the range of the characteristic local frequency $\omega_{SS}$ of the electron spin-spin reservoir (SSR). This coincidence, together with the electron-nuclear dipole-dipole interactions, leads to the thermal mixing (TM), that is, to equalizing the SSR temperature $T_{SS}$ with nuclear Zeeman temperature $T_{IZ}$ and thus to the corresponding increase in nuclear polarization $P_I = \tanh(h \omega_I / 2k_B T_{IZ})$. This process is illustrated in figure 3, where the energy spectrum of the SSR is represented as quasi-continuous bands which broaden the Zeeman sublevels of a paramagnetic center.

**Figure 3.** Diagram of the TM DNP mechanism (for the case of $T_{SS} < 0$). Horizontal segments reflect populations of corresponding energy levels in the electronic (left) and nuclear (right) systems. The arrows show transitions induced by the microwave pumping and I-S dipolar interactions.

As was shown by Provotorov [13], a strong decrease in $|T_{SS}|$ can be also achieved by saturation one of the EPR lines (a) coupled with the other one (b) with dipole-dipole cross-relaxation, the energy difference $\hbar(\omega^a - \omega^b)$ being transferred to (from) the SSR. This approach is fully applicable to the inhomogeneously broadened EPR line, when the cross-relaxation between spin packets is faster than spin-lattice relaxation and so leads to effective spectral diffusion throughout the line. Thus, this case is somewhat similar to homogeneous dipolar broadening.

The TM mechanism of DNP was firstly suggested by Kozhushner and Provotorov in 1964 [14]. Further development of the theory was performed by Buishvili [15], Borghini [16], Kozhushner [17] and others. Kozhushner [17] named this mechanism “Dynamical Cooling”, whereas in the West the term TM is commonly used. Systematic experiments dedicated to clearing up the role playing by the electron spin-spin temperature in DNP (and, generally, in EPR in solids) were carried out in the Moscow, Leiden and Saclay groups, see the review articles [18-22] and monographs [23, 24].

To get a deeper insight into the physical nature of the TM mechanism, let us consider the elementary act of thermal mixing, see figure 4. Here the flip-flop of two electron spins ($S_2$ and $S_3$) is accompanied by simultaneous flip of a nuclear spin $I$. Such a process is governed by the dipole-dipole operators like $\hat{S}_2 \cdot \hat{S}_3 \hat{I}^z$, the energy matching being provided by the equality $\omega_1 = \Delta_3$, where $\Delta_3'=\gamma_S$ is the difference of the local fields created on the $S_2$ and $S_3$ spins by one more electron spin $S_1$. Extending to the many-spin system, one can say that a portion of the SSR energy is transferred to the nuclear Zeeman subsystem, and vice versa. Thus, the thermal mixing can be considered as generalization of the 3-spin CE to real many-particle spin-spin interactions.

**Figure 4.** Elementary act of thermal mixing: simultaneous flips of the nuclear spin $I$ and electron spins $S_2$, $S_3$ in the local field of spin $S_1$ (the flux produced by $S_1$ is shown with dotted lines).
The spin temperature approach enables one to calculate the DNP enhancement by the method of thermal balance. The most convenient way is to consider the problem in the rotating reference frame (RF) which rotates about \( z \) axis at the frequency of microwave pumping, \( \omega_p = \omega_S + \Delta_p \), in the sense of the electronic Larmor precession [25]. The conversion to the RF is realized by means of the unitary operator \( \hat{U} = \exp(i \omega_p \hat{S}^z t) \) which acts on the electron Zeeman subsystem (SZ) only, the other ones being unaffected. In the RF, the frequency and, consequently, the spin temperature of the electron Zeeman system are multiplied by the factor of \(-\Delta_p/\omega_S\). As a result, the corresponding equilibrium temperature in the RF is as low as

\[
T_0^{RF} = -\frac{\Delta_p}{\omega_S} T_0
\]  

(3)

The corresponding block diagram is shown in figure 5.

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**Figure 5.** Thermal balance diagram of the Thermal Mixing DNP mechanism. The rotating reference frame for electron spins is used. The difference system (DS) is added in the case of inhomogeneous broadening of the EPR spectrum, see the text.

In the RF, there are two “lattice thermostatates”, one of them (strongly cooled) being coupled to SZ\(^{RF}\) with the relaxation rate \( T_{1S}^{-1} \), and another (at the equilibrium temperature \( T_0 \)) connected to the nuclear Zeeman system (IZ) and SSR with corresponding spin-lattice relaxation rates, \( T_{1I}^{-1} \) and \( T_{1SS}^{-1} \). The coupling between SZ and SSR is provided by the microwave pumping with the rate \( W_p \) of the resonant microwave absorption, and the thermal mixing between SSR and IZ occurs as discussed above with the rate \( W_{SSI} \). In the case of inhomogeneous EPR broadening with fast spectral diffusion, one more subsystem, the “difference” one (DS) should be added and coupled to the SSR with the rate \( W_{CR} \) of the SS cross-relaxation. Using these coupling rates and corresponding thermal capacities determined from characteristic frequencies and spin concentrations of the subsystems involved [23-25], one can calculate the steady state enhancement of nuclear polarization. In the high temperature approximation \((P_S << 1)\) one gets:
\[ E = \frac{-\omega_p \Delta_p}{\Delta_p^2 + M_{2,\text{inh}}^2 + a \omega_{SS} + f \omega_f^2} \]  

where \( M_{2,\text{inh}} \) is the second moment of the inhomogeneous EPR line; \( a = T_{1S}/T_{1SS} \), and \( f \) is the “leakage factor” accounting for extrinsic nuclear spin-lattice relaxation. According to equation (4), the maximum positive and negative enhancements are attainable at

\[ \Delta_p^{\text{max}} = \mp \left( M_{2,\text{inh}}^2 + a \omega_{SS} + f \omega_f^2 \right)^{1/2} \]

and amount to

\[ E_{\text{max}} = \frac{\omega_S}{2 \Delta_p^{\text{max}}} \]

When the SS cross-relaxation (spectral diffusion) inside the EPR spectrum is less effective, the microwave pumping produces a “burned hole” in the line contour. Corresponding calculations show [26] that, in the limiting case of very narrow “hole”, the \( E(\Delta_p) \) dependence resembles the derivative of the EPR absorption and thus can be asymmetric in some cases. Similar results were obtained for the 3-spin CE as well [21, 23].

To check the validity of the TM mechanism experimentally, two methods can be used. First, one can compare directly \( T_{SS} \) with \( T_{IZ} \). This approach was used in [27], where the \( SS \) temperature of Cr\(^{3+}\) paramagnetic ions in the \( \text{Al}_2\text{O}_3 \) crystal was determined from the asymmetric shape of the saturated EPR line and found to be equal to \( T_{IZ} \) of the \( ^{27}\text{Al} \) nuclei polarized at \( T_0 = 1.8 \) K and \( \omega_p/2\pi = 9.5 \) GHz. To our knowledge, this was the first experimental confirmation of the TM DNP mechanism. Later, similar evidences were demonstrated on various materials [28-30, 21, 22].

Another method consists in comparison of spin temperatures of different nuclei present in the same sample upon DNP. Such experiments were performed, for example, on \(^7\text{Li} \) and \(^{19}\text{F} \) nuclei in LiF crystals doped with paramagnetic defects \((T_0=0.74 \) K; \( H = 2.5 \) T) [31]. The Zeeman spin temperatures of different nuclei were found to be equal at the steady state, evidencing for the thermal mixing with SSR. Other examples can be found in references [18, 21, 23, 24].

Thus, to the end of the 20th Century, the thermal mixing was recognized as an efficient DNP mechanism working at low (helium) temperatures in materials used in polarized nuclear targets, as well as in nuclear ferro- and antiferromagnets elaborated by A. Abragam, M. Goldman and their collaborators [24]. By that time, the DNP studies seemed to be a rather completed field, not very attractive for further development. However, a sudden burst happened just at the start of the new Millennium.

Now, the main goal is a giant increase in NMR sensitivity combined with the most modern NMR techniques, such as magic-angle spinning (MAS), coherent multi-pulse methods, cross-polarization, 2D spectra, and so on. The success was achieved owing to new technical options, such as extremely high magnetic fields provided by superconducting magnets and, especially, powerful microwave sources in the short millimeter range, named gyrotrons, which supply up to 5 W c. w. in the range of 100-600 GHz. As a result, the DNP experiments became compatible with a rotor for magic-angle spinning and other modern NMR equipment. Of particular value is also the possibility of the EPR saturation not only at liquid helium, but at liquid nitrogen and even room temperatures as well.

Though the first attempts to combine the MAS NMR with DNP were realized as early as 1985 [32], the most successful DNP experiments in high magnetic fields were performed only recently by the group of R. G. Griffin, one of the leaders of the “new wave”. Since the author of this presentation did not participate in the recent DNP research (except for minor consulting and discussion), the consideration will be restricted to several impressive examples. More detailed information can be found
in the review articles [33, 34] and references therein, as well as in the special issues of the APMR and PCCP journals where these articles were published.

The most striking idea realized in recent years is the technique of temperature jump, named also the DNP-dissolution or hyperpolarization method. This technique, proposed firstly by Ardenkjaer-Larsen et al. [35], consists of three steps. First, high nuclear polarization is achieved by DNP at very low temperatures and high magnetic field. Then the polarized sample is extracted momentarily from the cryostate and melted with superheated water (or, alternatively, by \textit{in situ} laser irradiation [36]). And, finally, the liquid sample can be transported quickly, by pressured gas, to the MRI system, where the polarized solution is injected into the patient body. Surprisingly, the enhanced nuclear polarization remains nearly the same during the whole procedure, with the loss of 20-25% only. As a result, the effective enhancement relative to the equilibrium polarization at room temperature amounts to 50000, with the relaxation rate of the order of 1 minute. This allows to monitor the metabolism processes \textit{in vivo}, in particular, in cancer treatment.

Another line of inquiry relates to the combination of DNP with MAS NMR. A typical result obtained at 90 K and 5 T was presented by van der Wel et al. [37]. The object of study was a nanocrystalline peptide fragment; the sample was immersed in frozen alcohol doped with free radicals. The enhancement of proton polarization, \( E \approx 150 \), acquired in the polarizing medium, penetrated the peptide crystal due to spin diffusion and then was transferred to the \(^{13}\text{C} \) nuclei via the cross-polarization technique. As a result, the well-resolved 2D spectra of \(^{13}\text{C} \) were obtained. Another example relates to the \(^{15}\text{N} \) MAS NMR spectrum in bacterial rhodopsin taken at the same temperature and field [38]. Without DNP, a poor noisy trace was obtained after 3 days of accumulation, whereas an excellent spectra, including the 2D ones, were achieved with 30 minutes of accumulation under the DNP conditions. A giant increase of sensitivity is evident. Worthy of mention are also the DNP-enhanced \(^{1}\text{H} - ^{13}\text{C} \) solid-state NMR correlation spectroscopy [39], the DNP experiments in very high magnetic fields up to 14 T [40], and a lot of applications of DNP to biochemical and medical problems, see the above-cited Journals and references.

Now let us discuss on the dominant physical mechanisms of DNP as it looks today. Strong arguments in favour of the 3-spin CE were advanced recently by the Griffin group [33, 41]. They showed that the highest polarization enhancement for protons can be achieved with the use of biradicals, such as TOTAPOL biradical and others, which provide a splitting of the EPR line due to the intramolecular SS interaction between two unpaired electrons. The splitting was found to be of the order of the proton NMR frequency in the field of 5 T, thus favouring to the CE. A slight asymmetry in the \( E(\Delta \omega) \) dependence was observed for protons, thus evidencing against the effective spectral diffusion in the inhomogeneous EPR line, see equations (4) – (6). At the same time, the DNP experiments performed at liquid He temperatures on the samples containing \(^{1}\text{H} , ^{13}\text{C} , ^{6}\text{Li} \) and \(^{7}\text{Li} \) nuclei showed the equalizing of all nuclear spin temperatures, unambiguously pointing to the TM mechanism [42].

In fact, the dominance of one or another mechanism is determined by competition between spectral diffusion (SS cross relaxation) inside the inhomogeneous EPR line and electron spin-lattice relaxation. The TM mechanism dominates when the rate of SS cross relaxation between the spin packets separated by \( \omega_{\text{r}} \) exceeds the spin-lattice relaxation rate, \( w_{\text{CL}}(\omega_{\text{r}}) > T_{1S}^{-1} \). This condition seems to be fulfilled at low enough temperatures (slow spin-lattice relaxation) and/or for low NMR frequencies (low enough \( H \) or \( \gamma_{I} \)). Under the opposite condition, the 3-spin CE can be the most effective DNP mechanism, what is perhaps the case for the proton DNP at 90 K and 5 T [43]. Note, however, that the \( E(\Delta \omega) \) dependence observed on the \(^{13}\text{C} \) nuclei at the same experimental conditions [43], as well as for \(^{2}\text{H} \) DNP with the use of a radical with narrower EPR line [39], was found to be nearly symmetric and, according to our estimations, agrees qualitatively with the TM model. Anyway, an accurate comparison of the relative efficiency of the 3-spin CR and TM DNP mechanisms under realistic conditions seems to be of interest for further study. The quantum mechanical treatment presented by Hu \textit{et al.} [41] may be considered as the first step which should be proceeded with strict analysis of the relaxation and many-particle spin dynamics.
And, finally, a few words about future. It seems that the steep rising of DNP development is far from its finish. A lot of new methods and applications are knocking at the door, including the multi-pulse and rotating-frame techniques adopted from modern NMR [33] and revival of the classical Overhauser effect in liquids, now in extremely high fields [44]. The last but not least are the optical methods. In particular, the use of the optically excited paramagnetic triplet states in molecular crystals with DNP performed through the electron spin locking [45] is of considerable interest.

In conclusion, the DNP methods are on the steep rise, and new successes are prospective in near future.

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