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Dynamic nuclear polarization

Polarisation dynamique nucléaire

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ABSTRACT

Dynamic nuclear polarization, or DNP, refers to the increase of the polarization of nuclear spins in condensed matter, liquid or solid, coupled with electronic spins at low relative concentration, by inducing radio or microwave transitions at frequencies close to the electronic resonance frequency in the external magnetic field. Another described method relies on indirect optical pumping methods at temperatures close to room temperature for the nuclear polarization of rare gases. The various mechanisms of DNP are described in physical terms. This is followed by a succinct description of its main applications in various domains of physics, in chemistry and in medicine.

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R É S U M É

La polarisation nucléaire dynamique (en anglais DNP) se réfère à l'augmentation de la polarisation de spins nucléaires dans la matière condensée, liquide ou solide, couplés à des spins électroniques à faible concentration relative, en induisant des transitions radio ou micro-ondes de fréquence proche d'une fréquence de résonance électronique dans un champ magnétique extérieur. Une autre méthode décrite consiste en l'utilisation indirecte du pompage optique à température proche de la température ordinaire pour la polarisation nucléaire de gaz rares. Les divers mécanismes de polarisation sont décrits en termes physiques. Ceci est suivi d'une description succincte des principales applications de la DNP dans différents domaines de la physique, de la chimie et de la médecine.

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1. Introduction

The purpose of this article is to give a general description of the physical processes known under the general name of DNP, a short-hand notation for Dynamic Nuclear Polarization, their principle, their implementation, and their main applications and prospects.

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Emphasis is put throughout on the physical principles put to use, rather than on equations, kept to a minimum. More detailed and extensive treatments are available in the references.

The article is organized as follows.

Section 2 presents the essential aspects of Magnetic Resonance, mostly nuclear but also electronic, in a simplified form:

- principle, classical and then quantum descriptions of spin precession,
- interactions concerning nuclear spins, scalar, dipolar, chemical shifts, indirect, as well as electronuclear interactions,
- spin–lattice relaxation under the effect of these interactions,
- rotating frame,
- spin temperature,
- practice of magnetic resonance.

Section 3 describes DNP in the presence of motion, essentially in liquids and gases:

- cross-relaxation under dipolar or scalar interactions,
- case of electronic spins resonating in the hyperfine field of nearby nuclear spins, and application to the realization on an earth-field magnetometer,
- dynamic polarization of gases by indirect use of optical pumping.

Section 4 is devoted to the most important versions of DNP, that in non-conducting solids through its main mechanisms: the Solid Effect by excitation of the so-called forbidden electron–nucleus transition, and DNP by excitation of allowed electronic transitions leading to a cooling of the non-Zeeman electronic thermal reservoir and the thermal coupling of the latter with the nuclear Zeeman reservoir.

Section 5 finally describes a selection of important applications of DNP:

- in liquids – detection of objects via a change of the Earth’s magnetic field,
- in gases – use of polarized helium-3 for polarizing neutron beams or for Magnetic Resonance Imaging (MRI) of the lungs,
- in solids – nuclear and particle physics, nuclear magnetic ordering in high magnetic field –, and the new-born dissolution DNP: nuclear polarization in the solid state followed by dissolution in a liquid medium, so as to increase the sensitivity of high-resolution NMR or of MRI.

2. Essentials of magnetic resonance (for general references, see [1–4])

2.1. Zeeman interaction and the Larmor theorem

A large number of nuclei possess an intrinsic angular momentum $\hbar \mathbf{I}$, where \hbar is Planck’s constant divided by 2π and \mathbf{I} is their spin, where the spin number $I = |\mathbf{I}|$ is integer or half-integer. They also possess a dipolar magnetic moment $\boldsymbol{\mu}$ collinear with the spin:

$$\boldsymbol{\mu} = \gamma \hbar \mathbf{I} \quad (1)$$

where the factor γ , called the gyromagnetic ratio, is a characteristic of each nuclear isotope.

The interaction of this moment with an external magnetic field \mathbf{B} , the Zeeman interaction, corresponds to an energy:

$$E = -\boldsymbol{\mu} \cdot \mathbf{B} \quad (2)$$

A consequence of these equations is the celebrated Larmor theorem which describes the dynamics of evolution of the magnetic moment:

$$\frac{d}{dt} \boldsymbol{\mu} = \boldsymbol{\omega} \wedge \boldsymbol{\mu} \quad (3)$$

where the frequency is equal to:

$$\boldsymbol{\omega} = -\gamma \mathbf{B} \quad (4)$$

This corresponds to a precession of the magnetic moment around the field, when it is not aligned with the field.

The result is the same for the bulk magnetization of an ensemble of homonuclear spins $\mathbf{M} = \sum \boldsymbol{\mu}_i$.

Equation (3) is replaced by:

$$\frac{d}{dt} \mathbf{M} = \boldsymbol{\omega} \wedge \mathbf{M} \quad (5)$$

In practice, the magnetic field is the sum of a steady field \mathbf{B}_0 along the axis Oz, plus possibly a much smaller radiofrequency field \mathbf{B}_1 rotating at, or close to, the resonance frequency $\omega_0 = -\gamma B_0$ (see Subsection 2.6 on the practice of magnetic resonance).

The preceding results, obtained by a classical calculation, remain valid in a quantum treatment, with the provision that the magnetic moments are operators proportional to the spin. The latter being quantized, it results from Eq. (2) that the energy is also quantized. The energy is described by an operator called the Hamiltonian H . The resonance frequency is equal to the energy difference, divided by the Planck constant, of eigenstates of the Hamiltonian between which the rf field has non-zero matrix elements. The preceding considerations also apply to electronic spins, usually called \mathbf{S} . The main difference is that their gyromagnetic ratio is much larger than the nuclear ones. For instance, for radicals and protons, the ratio is approximately: $\gamma_e/\gamma_p \approx 658$.

2.2. Spin–spin interactions

- Ever present are the dipole–dipole interactions. For two spins j and k , the corresponding Hamiltonian is of the form:

$$H_{Djk} = \frac{\gamma_j \gamma_k \hbar^2}{r_{jk}^3} \{ \mathbf{I}_j \cdot \mathbf{I}_k - 3(\mathbf{I}_j \cdot \mathbf{n}_{jk})(\mathbf{I}_k \cdot \mathbf{n}_{jk}) \} \quad (6)$$

where \mathbf{n}_{jk} is the unit vector joining the spins.

- The Fermi contact interaction between a nuclear spin \mathbf{I} and an electronic spin \mathbf{S} is of the form:

$$H_{\text{contact}} = J \mathbf{I} \cdot \mathbf{S} \quad (7)$$

- The indirect interaction between nuclear nearby spins in a molecule is mediated by the diamagnetic electronic environment. Very important for chemistry, they play no role in DNP. For completeness, let us cite the shielding interaction between a nuclear spin and the diamagnetic electron environment, yielding a frequency shift known as the chemical shift.

2.3. Spin–lattice relaxation

The spins are not isolated but coupled with the orbital degrees of freedom of the condensed matter in which they are embedded. The latter are called the lattice. The evolution of the spin statistical state towards equilibrium with the lattice is called spin–lattice relaxation. In most cases, the heat capacity of the lattice is practically infinite compared to that of the spins. It is often a good approximation to treat the lattice classically and to treat the spin–lattice coupling as randomly varying as a function of time. Examples are:

- modulation of the dipole–dipole interactions by rotational diffusion of the molecules or of inter-spin distance between nearby molecules, in liquids,
- modulation of contact interactions by exchange of electron–nucleus partners,
- lattice vibrations in solids modulating the coupling of the electronic spins, a major relaxation mechanism for the latter.

A consequence of the fact that the lattice is at a given temperature is that nuclear magnetization relaxes towards its thermal equilibrium value along the external magnetic field at the lattice temperature. The coupling of the nuclear spins with the lattice is weak and the nuclear relaxation time is long, from a fraction of a second to hours.

There are various types of spin relaxation, those of the magnetization components, parallel and perpendicular to the main field, respectively called the longitudinal and transverse spin–lattice relaxation with respective time constants T_1 and T_2 , those of the spin–spin interactions plus a few others of no concern in the present article.

Another type of evolution of the spin system, distinct from spin–lattice relaxation and observed in solid samples is the evolution towards an internal steady state of spins initially out of equilibrium, under the effect of the spin–spin interactions. The most conspicuous example is the evolution towards zero of magnetization normal to the external steady field. This is called spin–spin relaxation and its decay characteristic time is usually also called T_2 , although this decay is generally non-exponential. The decay time, loosely defined, is by many orders of magnitude shorter than the spin–lattice relaxation times: of the order of a few tens of microseconds, rather than a fraction of a second to hours for real spin–lattice relaxation.

2.4. The rotating frame

The fact that the magnetization that is not aligned with the static field is rotating around it at the frequency ω_0 shows up by the time variation of its components along the axes Ox and Oy *in the laboratory frame*. Let us project the magnetization components on axes OX and OY normal to Oz, but rotating at the frequency ω around the field B_0 , corresponding to the so-called rotating frame picture. The time evolution of the magnetization components along these axes corresponds to a rotation frequency:

$$\Delta = \omega_0 - \omega \quad (8)$$

which would be due to an apparent (or effective) longitudinal field:

$$B_{\text{eff}} = -\Delta/\gamma \quad (9)$$

If a transverse rf field of magnitude B_1 , corresponding to a Larmor frequency

$$\omega_1 = -\gamma B_1 \quad (10)$$

is rotating at frequency ω , it looks static in the rotating frame. Then, the evolution of the magnetization, as seen in the rotating frame, is the same as in an applied *static* field of components B_{eff} and B_1 , that is, of Larmor frequency components Δ and ω_1 . There lies one of the main interests of the rotating frame picture.

In particular, even in the absence of rf irradiation, the evolution of the magnetization in the frame rotating at frequency ω_0 is the same as in the absence of any applied field. The magnetization evolution is then solely due to spin relaxation.

The rotating frame concept can be extended to more complex situations, for instance to the case when there are two nuclear spin systems, say I and S , of respective gyromagnetic ratios γ_I and γ_S . One may then use projections on axes rotating at different frequencies for each spin species and adjust at will the effective longitudinal fields for each species.

By replacing the rotating fields with apparent static fields, the rotating frame picture brings about a substantial simplification in the description of the spin evolutions.

In a quantum treatment, the passage to the rotating frame corresponds to a so-called change of representation, and the geometric picture of a rotation is limited to the case of a purely Zeeman interaction, that is, to a main Hamiltonian corresponding to an energy of the form (2).

Things are different for, say, the quadrupole interaction of the nuclear spins with the electric field gradient produced by a non-isotropic environment. Limited to spins larger than $1/2$, it is quadratic in the spin operator. In the simplest case of an axially symmetric field gradient, the corresponding Hamiltonian in zero external field is of the form:

$$H = A\{I_z^2 - I(I+1)/3\} \quad (11)$$

When using an irradiation at a frequency close to a quadrupole resonance frequency, one may again express the effective Hamiltonian in a time-independent form through an appropriate quantum change of representation, which does not correspond to a rotation, and for which there is no simple geometric picture. The only appropriate description is then purely quantum-mechanical, but otherwise very similar to the Zeeman case, and one may refer to a pseudo-rotating frame. Very little reference to quadrupole interactions will be made in the following.

2.5. Spin temperature (for general references, see [1] and [3])

The first non-trivial introduction of the spin temperature concept was made as a result of a series of experiments, the most important ones being those listed below.

- The observation by Pound [5] that, following the demagnetization to zero field and then re-magnetization of a solid sample of LiF, the NMR signal was recovered, with a relaxation time in zero field orders of magnitude longer than the solid-state one T_2 . Furthermore, when inverting the polarization prior to the passage through zero field, the NMR signal after re-magnetization was also inverted (Purcell and Pound [6]). They tentatively interpreted these results by the hypothesis of a spin temperature down to zero field, that is, a Boltzmann distribution of populations among the energy levels of the interactions. Whereas such a distribution was clear for the Zeeman levels in high field, it was far from evident for the spin-spin interactions, essentially dipolar, whose spectrum is quasi-continuous and unknown in detail, in zero field. For the case of an initially inverted magnetization, they introduced the concept of a negative spin temperature: at negative temperature, the higher the energy of the levels, the larger their populations. This is possible for spin systems, in contradistinction with usual systems, because their energy spectrum has an upper bound as well as a lower bound.
- Abragam and Proctor [7] showed that the same NMR signal was observed in high field, whether the sample was subjected to a slow demagnetization-remagnetization cycle or cooled in a liquid helium bath in zero or low field and allowed to reach a steady state, thus ascertaining the actual existence of the spin temperature. The results were in quantitative agreement with the hypothesis of a spin temperature during the demagnetization-remagnetization process that was adiabatic, in the sense of isentropic. Demagnetization corresponds to a decrease in the absolute value of the spin temperature, conventionally called cooling whatever the sign of the spin temperature.
- Redfield [8] interpreted anomalous signal saturations under rf irradiation close to resonance by the establishment of a Boltzmann distribution of populations among the energy levels of the effective interactions, Zeeman and spin-spin, in the rotating frame. This has since been known as “spin temperature in the rotating frame”, an expression introduced by Abragam.

Several remarks are in order about spin temperature in the rotating frame in high dc field.

Firstly, the only effective spin–spin interactions are those connecting degenerate Zeeman levels, that is, those that remain time-independent in the rotating frame, the so-called secular interactions. The non-secular ones are much smaller than the energy difference, in the laboratory frame, between states they connect, ω_0 or $2\omega_0$, and their effects on eigenstates and energies are small and can be neglected. The energies are expressed in terms of frequencies:

$$\Delta\omega = \Delta E/\hbar$$

For a pair of homonuclear spins, of same γ , at an angle θ from the axis Oz, the secular part of the dipolar interaction (6) is:

$$H'_{Djk} = -\frac{\gamma^2\hbar^2}{r^3} \frac{1}{2} (3\cos^2\theta - 1) \{3I_{jz}I_{kz} - \mathbf{I}_j \cdot \mathbf{I}_k\} \quad (12)$$

As for a scalar product as in Equation (7), it is invariant by rotation and is therefore secular.

For unlike spins, with different values of γ , that is, different Larmor frequencies, the secular part of their interaction is that proportional to $I_z S_z$.

The second remark is about a spin system suddenly subjected to an off-resonance irradiation of small amplitude:

- if the irradiation frequency is below the Larmor frequency, the effective longitudinal frequency Δ is, according to Equation (8), of the same sign as the Larmor frequency ω_0 , and the spin temperature in the rotating frame has the same sign as in the laboratory frame, usually positive;
- if the irradiation frequency is above the Larmor frequency, the sign of the spin temperature in the rotating frame is opposite to that in the laboratory frame, i.e. usually negative.

The signs remain the same if the rf frequency is adiabatically swept down to resonance and are then those of the secular interactions. Extensive applications are described in Section 5.2.

The final remark is that, if after rf irradiation and achievement of a spin temperature in the rotating frame the rf field is switched off, there is no reason to remain in the rotating frame picture. Back to the laboratory frame, with sudden jump from effective to real Zeeman interaction, which involves no change in the state of the spin system, one must ascribe different temperatures to the Zeeman part and to the spin–spin part of the interactions. These parts are no longer in thermal contact, so that they constitute different constants of the motion. Therefore, they evolve independently, in particular as regards their spin–lattice relaxation.

2.6. Practice of magnetic resonance

We consider briefly how the rf irradiation is performed and how the magnetic signal is recorded.

If the rf field is applied in CW form and is sufficiently small not to perturb substantially the spin system, it gives rise to a small transverse magnetization, which is detected. Starting with a simple nuclear magnetization, the component in quadrature with the rf field is absorption, and during a linear sweep through resonance, it follows a bell-shaped curve. The component in phase with the rf field is dispersion, which, during a sweep through the line, has the form of the derivative of a bell-shaped curve.

For a larger rf field amplitude, the sweep through the line corresponds to an adiabatic magnetization–demagnetization–remagnetization whose final result is a reversal of the initial magnetization, provided the duration of the sweep is short compared with the relaxation times. This is known as a fast passage. The transverse magnetization component is practically in phase with the rf field.

By contradistinction, one may apply a rf field of magnitude much larger than the resonance width, say, at the resonance frequency. Then, in the rotating frame, the effective field is purely transverse, and the evolution of the spins is a precession around this field. If stopped when the precession angle is equal to θ , it corresponds to a so-called θ pulse. After a $\pi/2$ pulse, the magnetization is purely transverse, and one can detect and follow its decrease as a function of time. It can be shown that this free induction decay, in short FID, is the Fourier transform of the CW signal. The use of pulses, recording of FID signals and computation of their Fourier transform has practically superseded the CW observation since the advent of the “numeric era” for computers, because of the enormous time saving it provides, and the ever-increasing variety of sophisticated excitation–observation methods it gives rise to.

3. Dynamical nuclear polarization under motion (for general references, see [1], [9–16])

The motion refers as a rule to the relative change of position of the spins between which the DNP takes place, most of the time nuclear and electronic spins: paramagnetic centres at low concentration in liquids or coupling between conduction electrons with fixed nuclei in metals. This last case is mostly, although not entirely, of limited practical interest, and it will be described in this perspective. The polarization of gases by the way of optical pumping uses tools of a different nature and is treated in a separated sub-section.

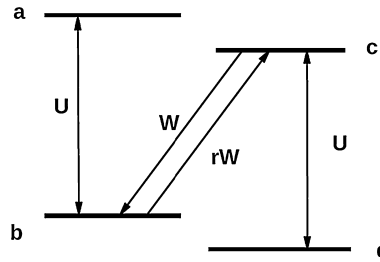


Fig. 1. Overhauser Effect. Schematic transitions within an electronic and a nuclear system. The saturation irradiation transitions between pure electronic states a and b, and c and d, of equal rates U for up-to-down and down-to-up transitions equalize their populations. The “skew” transitions between mixed electronic-nuclear states b and c have different rates W and rW , where r is the Boltzmann factor of Eq. (15).

3.1. The Overhauser Effect

In 1953, at a meeting of the American Physical Society, a young physicist, A.W. Overhauser, presented his theoretical prediction that saturating the electron resonance of conduction electrons in a metal by microwave irradiation at their resonance frequency resulted in an increase of the nuclear polarization to the same value as if their resonance frequency were equal to that of the electrons [9]. This prediction met with complete scepticism from most of the NMR authorities in the audience, until it was experimentally verified the same year by Carver and Slichter [10]. This effect, together with its generalizations, was to remain known as the “Overhauser Effect” and the prototype of all DNP mechanisms.

The gist of the effect is the nuclear relaxation by the transient contact interaction of the form (7) between the nuclear spins and the conduction electrons, which occurs via “flip-flop” transitions. Its description will be made through Fig. 1 for the case of a nuclear spin $1/2$.

The states correspond, say, to the following electron and nuclear spin states:

$$a = |+, +\rangle, \quad b = |-, +\rangle, \quad c = |+, -\rangle, \quad d = |-, -\rangle \quad (13)$$

The microwave excitation at the electronic frequency saturates the electronic resonance with rate U much larger than the thermal transition rates, that is, it equalizes the populations of a and b, and of c and d.

In metals, the nuclear spin–lattice relaxation is produced by the time modulation of the contact interaction of the form (7) between the fixed nuclei and the moving conduction electrons. The scalar product can be written under the form:

$$\mathbf{I} \cdot \mathbf{S} = I_z S_z + \frac{1}{2}(I_+ S_- + I_- S_+) \quad (14)$$

so that the nuclear relaxation takes place via transitions between states b and c, with rates W from c to b and rW from b to c, where:

$$r = \exp[-h(\omega_S - \omega_I)/kT_L] \quad (15)$$

is the Boltzmann ratio for the frequency of the transition and the lattice temperature T_L .

Therefore, in the steady state, we will have the following relations between the populations of the various states:

$$P(c) = P(d) = rP(a) = rP(b) \quad (16)$$

or else:

$$P(c) + P(d) = r(P(a) + P(b)) \quad (17)$$

which, according to Eq. (15), (nearly) proves Overhauser’s statement that the nuclear polarization is increased (in absolute value) to the thermal equilibrium value corresponding to the electronic resonance frequency ω_S , an excellent approximation since it is so much larger than ω_I , the nuclear one.

3.2. The Solomon equations [11,12]

Solomon performed an extensive study of relaxation in liquid hydrofluoric acid HF, both experimental and theoretical.

His main result was the discovery of cross-relaxation between the two nuclear species, with characteristics depending among other factors on the nature of the internuclear time-dependent interaction.

Let us now call I and S the two kinds of nuclear spins. The time evolution of their expectation values (proportional to their magnetization) along the direction of the magnetic field is given by equations of the form (Solomon’s notations):

$$\frac{d}{dt}\langle I_z \rangle = -\rho(\langle I_z \rangle - I_L) - \sigma(\langle S_z \rangle - S_L) \quad (18)$$

where I_L and S_L are the thermal equilibrium values, and a similar one for the spin S . These are the Solomon equations.

In particular, when, say, the spins S are saturated, the steady-state value of the spin I expectation value is:

$$\langle I_z \rangle_{\text{steady}} = I_L + (\sigma/\rho)S_L \quad (19)$$

This provides an explanation for the Overhauser Effect: it is nothing else than the result of cross-relaxation between the nuclear spins and the electronic ones. It is not limited to metals, but it is also effective in liquids.

When the spins S are electronic spins at low concentration in a liquid, their coupling with the lattice is in general the dominant factor contributing to their spin–lattice relaxation.

Furthermore, despite their low concentration, they relax all nuclear spins, since each one comes repeatedly close to electronic spins through their Brownian motion.

The calculated value of the ratio (σ/ρ) is equal to -1 for relaxation by scalar interactions and to $1/2$ for relaxation by dipole–dipole interactions. In this last case, relaxation transitions take place between states a and d as well as between b and c.

Both cases were met with hydrofluoric acid:

- in very dry samples, the time-dependent interaction is the dipole–dipole one, modulated by rotational molecular Brownian, whence $(\sigma/\rho) = 1/2$;
- in samples containing a small amount of water, a chemical exchange takes place between the protons of HF and those of water, which modulates the scalar indirect interaction between H and F. This modulation dominates the nuclear relaxation, whence $(\sigma/\rho) = -1$.

3.3. The Earth's field magnetometer [13]

Certain free radicals experience a hyperfine interaction between the electron spin and a nearby nuclear spin in the same molecule, of the form (7) for its scalar part, invariant by rotation. This is the case for nitroso free radicals, where the nucleus coupled with the electron is nitrogen ^{14}N , of spin 1. In zero field, this interaction splits the level manifold into two sets, whose splitting Ω is of several tens of MHz. In low field, such as the Earth's magnetic field, these are slightly split, and the electronic resonance spectrum consists of several lines. When in solution at low concentration in water or in a proton-rich solvent, the saturation of one line increases the proton polarization by a large factor, determined by the ratio of Ω to the proton's Larmor frequency. The saturation of one of these lines yields a negative proton polarization, that is, a magnetization antiparallel to the field, of such magnitude that it is possible to realize a maser, that is, an auto-oscillator at the Larmor frequency of the protons in the Earth's magnetic field. The accurate measurement of the oscillation period (or frequency) yields the value of this field with an experimental accuracy of about 10^{-6} . This magnetometer is very simple, it does not require sophisticated electronics nor high electric power and it works at room temperature with no need of thermal regulation. Several of its applications are described in the last section.

3.4. Dynamic polarization making use of optical pumping [14–16]

This nuclear polarization procedure works on gases. It is an indirect process leading eventually to the nuclear polarization of rare gases, essentially helium-3, but also xenon-129, for practical applications. Its main characteristics is that it yields nuclear polarizations close to unity while performed at temperature close to room temperature and most of the time in low external magnetic field.

It exists under two different variants, schematically described below for the specific case of ^3He .

The first one, dubbed SEOP, for “spin exchange optical pumping”, is due to Bouchiat et al. [14].

It uses a mixture of Rb (sometimes Rb–K) atoms with ^3He atoms, in gaseous form, at a temperature adjusted so as to obtain the desired Rb vapour pressure. It consists in irradiating the Rb atoms by resonant circularly polarized laser light, so as to promote them to a polarized excited state with non-zero angular momentum: $\langle L_z \neq 0 \rangle$. Thanks to spin–orbit coupling, this angular momentum is shared with the Rb electronic spins. The following collision-induced decay to the ground state leads to an accumulation of Rb atoms in a spin-polarized state. The net result is the production of a Rb atomic gas of high electronic polarization.

This polarization is transferred to the nuclear spins of the ^3He surrounding gas as follows. During collisions between ^3He and Rb atoms, there exists a transient contact interaction of the form (7) between their respective spins. This produces a cross-relaxation between these spins identical to that described by the Solomon equations (18), with $\sigma/\rho = -1$.

Under continuous laser optical pumping and cross-relaxation, the steady-state nuclear polarization reaches a value corresponding to

$$\langle I_z \rangle_{\text{eq.}} = I_L + \langle S_z \rangle - S_L \gg \langle S_z \rangle \quad (20)$$

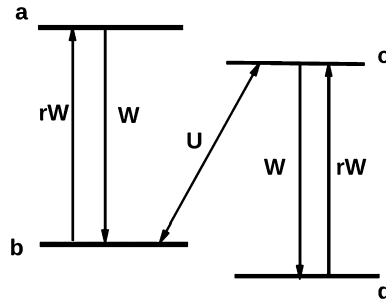


Fig. 2. Solid effect. Schematic transitions within an electronic and a nuclear system. The saturation irradiation between mixed electronic-nuclear states b and c, of equal rates U for up-to-down and down-to-up transitions equalize their populations. The relaxation transitions between pure electronic states a and b, and c and d, have different rates W and rW for up-to-down and down-to-up transitions, where r is the Boltzmann factor of Eq. (22).

that is, close to unity. In practice, nuclear relaxation by additional mechanisms (“leakage” relaxation) limits the nuclear polarization to a somewhat smaller value.

The second variant, dubbed MEOP, for “metastability exchange optical pumping”, is due to Colegrove et al. [15].

It uses pure ^3He most of the time, but also ^3He - ^4He mixtures. It is performed in two steps. The first one is to promote the ^3He atoms to a metastable state by an electrical discharge. In a second step, circularly polarized laser light is applied to perform the optical pumping on these metastable atoms. During subsequent collisions with atoms in the ground state, a metastability exchange takes place between a metastable optically pumped atom and an atom in the ground state. The net result is to enrich the ground state with spin-polarized ^3He gas.

The many variants, experimental implementations, and applications are described in a review article by Gentile et al. [16].

4. Dynamic nuclear polarization in solids (for general references, see [1,17–19])

In solids, with electronic spins at low concentration (often called impurities, even when improperly), their coupling with crystalline vibrations is responsible for the random fluctuation of their longitudinal component S_z , as well as for their spin–lattice relaxation.

As for the spin–lattice relaxation of a nuclear spin I_j by an electronic spin S_k , it takes place most of the time via the modulation of the longitudinal component of the electronic spin, through the part of their dipole–dipole interaction of the form:

$$H_{jk}(t) = \frac{\xi}{r_{jk}^3} S_{kz}(t) I_{j\pm} \quad (21)$$

only effective for nuclear spins close to an impurity.

The spin–lattice relaxation of the whole sample is ensured by spin diffusion from these spins close to impurities towards the bulk of the nuclear spins, via the internuclear dipole–dipole interactions [1].

It is evident from the form of Eq. (21) that saturation of the electronic spins is unable to modify the nuclear polarization, so that other irradiation strategies are to be used. The appropriate one turns out to be a microwave irradiation not at the electronic resonance frequency, but in its vicinity. Two different mechanisms have been put to use. One is the Solid Effect, so named to clearly insist on the difference with the Overhauser Effect. The second one is thermal mixing, often simply called DNP. We describe both in turn.

4.1. The Solid Effect

The method of dynamic polarization known as the Solid Effect has been invented twice, independently and at short time intervals, by Jeffries [20] and by Abragam and Proctor [21].

It consists in irradiating the sample at a frequency equal to the electronic resonance frequency *plus* or *minus* the nuclear resonance frequency.

This is illustrated in Fig. 2. It resembles Fig. 1 very much, except that:

- irradiation is between states b and c at, say, frequency $\omega_S - \omega_I$, the electronic minus the nuclear resonance frequencies, producing an equalization of the populations of these two states, because of equal rates induced by the irradiation for the transitions from b to c as from c to b;
- no irradiation at the electronic frequency, resulting in different transition rates, induced by the spin–lattice coupling, for up-to-down transitions and for down-to-up ones, the ratio being here:

$$r = \exp(-h\omega_S/kT_I) \quad (22)$$

The populations in the steady state are:

$$P(b) = P(c) = rP(d) = P(a)/r \quad (23)$$

or else:

$$P(a) + P(b) = r(P(c) + P(d)) \quad (24)$$

With the choice of Eq. (13), the steady-state value of the nuclear polarization is equal to the thermal equilibrium value of the electronic one.

It is also possible to irradiate at the frequency $\omega_S + \omega_I$, that is, between states a and d. This would result in a steady-state nuclear polarization of the same magnitude as the electronic thermal equilibrium value, but of opposite sign. Thus, it is possible, by the Solid Effect, to produce at will large nuclear polarizations of either sign, a definite advantage for applications, as will be described in the last section.

It should be noted that a radio-frequency or microwave field perpendicular to the static field and acting only on one spin species, say electronic or nuclear, has no matrix element between states b and c, or a and d, so that the transitions between these states are produced by a second-order process. Therefore, the saturation of such a transition requires a relatively large irradiation field.

The Solid Effect has proved to be very effective when the width of the electronic resonance is smaller than the nuclear resonance frequency, the so-called well-resolved Solid Effect. The case when the linewidth is larger than the nuclear frequency raises a different problem. The case still relevant to the Solid Effect is that due to inhomogeneous broadening, i.e. when the ESR (Electron Spin Resonance) line consists of narrow homogeneous packets with no or little spectral diffusion through the line. In this case, DNP is described as a differential Solid Effect: the spin packets at $+\omega_I$ and $-\omega_I$ from the irradiation frequency contribute to positive and negative nuclear polarization, respectively, and the net polarization results from a differential effect due to the different magnitude of the two packets. This was the usual interpretation, correct in some instances, but a different one turned out to be necessary in many other cases, corresponding to a different mechanism, the thermal mixing to be analysed next.

4.2. Thermal mixing

The emergence of thermal mixing as a mechanism of DNP was unexpectedly initiated by the following experiment (Goldman and Landesman [22–24]).

- An rf field was applied in zero field at a frequency close to the quadrupole resonance frequency Ω_Q of ^{35}Cl in paradichlorobenzene;
- The rf field was switched off, then an external field was switched on adiabatically up to a few mT; as a result, a large proton resonance signal was observed on the run.

As a function of irradiation frequency in zero field, the “polarization curve” of the proton takes the form of the derivative of a bell-shaped curve centred on the quadrupole resonance frequency.

The interpretation was based on the analogy with the irradiation of nuclear spins close to their Larmor resonance frequency in an external field, described in Section 2.5, that is, the establishment of a spin temperature in the frame rotating at the irradiation frequency, involving the effective Zeeman interaction and the secular spin–spin interactions, which results in a cooling of the latter.

In the present case, the quadrupole interaction plays the same role as the Zeeman interaction referred to above, and the role of the effective Zeeman interaction is replaced by an effective quadrupole interaction of frequency equal to the difference between the irradiation frequency and that of the actual quadrupole resonance frequency.

The experiment was repeated in a small external field. One observed separately the thermal mixing curve for irradiation around Ω_Q and those of the Solid Effect for irradiation applied around $\Omega_Q \pm \omega_I$.

The remarkable fact was that these two effects were well separated, i.e. the thermal-mixing “peak”, was much narrower than the proton Zeeman frequency, by a factor five or more. This meant that the thermal mixing between nuclear Zeeman and spin–spin interactions was effective up to values of the nuclear Zeeman frequency substantially larger than the spin–spin interaction frequency width.

This experimental fact served as an incentive for Solomon to interpret unresolved DNP as a thermal mixing in two steps [25]. The first one, induced by the microwave irradiation, is between the effective electronic Zeeman interaction and the electronic non-Zeeman interaction, i.e. electron–nucleus dipole–dipole plus inhomogeneous broadening if present and not too large. The second one, taking place without intervention of the microwave field, is between the electronic non-Zeeman interaction and the nuclear Zeeman interactions of the bulk.

This interpretation was based on two assumptions that are far from evident:

- 1) that a spin temperature establishes within the electronic system even for very dilute electronic spins;

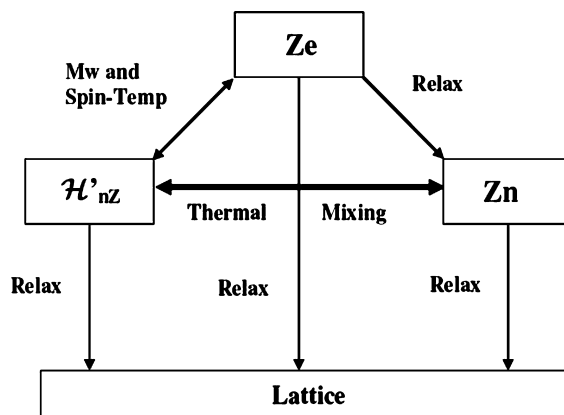


Fig. 3. DNP by thermal mixing. Schematic set of transitions within the system:

- microwave-induced thermal mixing between the effective electronic Zeeman term in the rotating frame and the secular electronic non-Zeeman term, leading to the establishment of a spin temperature,
- mixing between the electronic non-Zeeman and the bulk nuclear Zeeman terms, leading to a common spin temperature,
- nuclear relaxation of the bulk nuclear Zeeman term by the time-dependent part of the electronic Zeeman term,
- coupling of the various interactions terms with the lattice. (For the nuclear Zeeman term, it produces a spin–lattice leakage relaxation in addition to the main one: from nuclear-Zeeman-to-electronic-Zeeman-to-lattice.)

2) that the second mixing may take place even when the nuclear Zeeman frequency is distinctly larger than the EPR linewidth.

Both propositions could be proved later on by experiment and by theory, as exemplified in Refs. [26–29]. The second mixing, that is, the very existence of DNP by thermal mixing, requires that the distance of minimum approach between electronic impurities be sufficiently small.

The advantages of thermal-mixing DNP are that it involves allowed microwave transitions, which requires less microwave power than the Solid Effect, and that it is able to yield a nuclear polarization larger than that corresponding to the electronic resonance frequency.

That a thermal mixing was actually at work, rather than a differential Solid Effect, could be experimentally ascertained in a great number of cases of DNP.

The various mixings together with spin–lattice relaxation paths are shown in Fig. 3.

5. Applications of DNP

We limit the description to some of them, in general terms and without extensive references, merely as illustrations of the wealth and variety of the usefulness of DNP.

5.1. The case of liquids

We consider but two of them: cross-relaxation between nuclear spins, and the proton maser in the earth field.

Cross-relaxation, as described by the Solomon equations, is one of the major tools of NMR in chemistry (see, e.g., Ref. [4]). The magnitude of cross-relaxation between nuclear spins with different chemical shifts, measured most of the time by a two-dimensional spectroscopy method, gives a direct access to the proximity in space of the atoms involved. Together with the determination of their proximity along the molecule they belong to through their indirect interactions, they give access, among others, to the three-dimensional structure of large molecule such as proteins, a major goal in present-day biochemistry.

Measurement of the Earth's field by the proton maser is used, first, in geomagnetism. The short time it requires to perform a measurement affords the possibility to follow variations of this field on a time scale of about one second.

The second important application is the detection, through the change they produce on this field, of hidden ferromagnetic masses, such as lost underground gas pipes, submarines immersed at sea, even below the polar ice, first stages of Ariane space-rockets fallen into the sea, etc.

A particular mention must be made of the discovery by this magnetometer of the wreck of the frigate *La Méduse*, loaded with the 50 tons of its cannons on board, sunk off the shore of Mauritania in 1816. The worldwide memory of this dramatic wreck is primarily due to the famous painting of 1819 by Theodore Gericault *Le Radeau de La Méduse* (*The Raft of the Medusa*).

The search for the sunken ship was performed by an official department of marine archaeology, and the success of this endeavour, as well as the recovery and analysis of all the remnants of the ship provided information of great interest, both as regards the detection methods as for marine archaeology itself.

5.2. The case of solids

The foremost application of DNP is the production of polarized targets for nuclear and particle physics. The reason is that the scattering of particles by nuclei depends on the orientation of their spin. In this respect, it is important to use both spin orientations, a definite advantage of the Solid Effect as well as of thermal mixing.

The interest in polarized targets has somewhat diminished since the increasing use of colliding beams for very high-energy physics. There are still some important uses, such as for instance for the study of the spin structure of the nucleons.

Another very important application has been the production and study of nuclear magnetic ordering in high field. A high nuclear polarization corresponds to a low entropy. It is possible to transfer this Zeeman order to the spin-spin reservoir by adiabatic demagnetization. Rather than lowering the applied field to zero, one can perform the order transfer in high field by so-called adiabatic demagnetization in the rotating frame. For so doing, one applies an rf field far from resonance and makes the frequency offset decrease slowly either by sweeping the external field or the rf field frequency. This practice offers a number of characteristics, briefly touched upon in Section 2.5.

- If the initial rf frequency is below the resonance frequency, the spin temperature is positive, that is, the states of the spin-spin reservoir have larger populations the lower their energy. It is the opposite if the sweep starts above resonance: the spin temperature is negative, that is, the states have larger populations the higher their energy. After demagnetization, the rf field is turned off and the spin-spin interactions and the Zeeman interaction are decoupled, and their spin temperatures are different. The spin-spin temperature at order transition is in the sub-micro Kelvin range, whereas the Zeeman temperature is that of the lattice, that is, in the Kelvin range.
- The effective spin-spin interactions are not the full interactions, but only that part that commutes with the Zeeman term. In a single crystal, the form of this “secular” part depends on the orientation of the external field with respect to the crystalline axes. The simplest case, the most commonly studied, is that of purely dipole-dipole interactions, which are perfectly known. This double freedom – choice of the sign of the spin temperature and of the crystal orientation – makes it possible to produce a series of different magnetic structures: antiferromagnetic, several of them, ferromagnetic with domains, or transverse helical.
- It is possible to study these ordered structures by NMR since the external field is high. One can also use neutron diffraction, thanks to the fact that the spin-dependent part of the neutron-nucleus scattering amplitude, due to the strong interactions, can be, and is often, much larger than the magnetic one.

The interested reader will find general references for nuclear magnetic ordering in Refs. [30–32].

Another major application of DNP, of recent emergence, is the so-called Dissolution-DNP.

Dynamic polarization is produced at low temperature on a solid sample containing the desired molecules. The sample is then liquefied and transferred to the appropriate spectrometer for observing NMR. The main interest is to increase by an enormous factor the NMR signal, either in high-resolution NMR, so as to enable one to use very small amounts of the desired chemical or to observe other nuclei than protons, or in Magnetic Resonance Imaging (MRI), essentially medical, for faster imaging, or to observe small body parts.

A recent review on the subject can be found in Ref. [33].

5.3. The case of gases

It refers most of the case to polarized ^3He gas, either by the SEOP or the MEOP method. It is extensively used for a number of applications, which fall into several categories, among those listed below.

- *Fundamental physical properties of ^3He*
 - use of polarized ^3He targets as a substitute for neutrons in scattering of electron, proton or pion beams, providing information on neutron electric and magnetic form factors, that is, charge and magnetization distributions;
 - measurement of the spin-dependent scattering length of ^3He on nuclei.
- *Neutron spin filter*
 - The absorption of neutrons by ^3He depends on the relative orientation of their spin: orders of magnitude larger for antiparallel spins than for parallel spins. As a consequence, when a beam of neutrons passes through an adequate target of polarized ^3He , there is an absorption of their unwanted spin state, and the outgoing beam consists of polarized neutrons. This method can be used either to polarize an incoming beam of neutrons, or else to measure the polarization of a neutron beam. Neutron spin filters are versatile tools for many neutron physics experiments, such as the search for parity violations in scattering experiments, the study of neutron β -decay, etc., as well as for practical applications.
- Earth field magnetometers using optical pumping of gases, whose sensitivity is by an order of magnitude larger than the one with the proton maser. The various types have different specificities, which determine which one is used for a particular application. They will not be described in this article.

- **Magnetic Resonance Imaging with polarized ^3He or ^{129}Xe gas**
 - The study of Magnetic Resonance Imaging with polarized ^3He gas has acquired importance in medical research for the imaging of the lungs, hardly achievable by any other method. The fact that the gas is polarized is essential for providing enough signal for short-time imaging. The use of ^{129}Xe gas polarized by the SEOP method constitutes an important alternative to the use of ^3He for MRI. These methods are still at an experimental stage.

A recent review on these applications, already referred to for the polarization methods, can be found in Ref. [16].

References

- [1] A. Abragam, *The Principles of Nuclear Magnetism*, Oxford University Press, Oxford, UK, 1961.
- [2] C.P. Slichter, *Principles of Magnetic Resonance*, 3rd edition, Springer-Verlag, Berlin, 1990.
- [3] M. Goldman, *Spin Temperature and Nuclear Magnetic Resonance in Solids*, Oxford University Press, Oxford, UK, 1970.
- [4] M. Goldman, *Quantum Description of High-Resolution NMR in Liquids*, Oxford University Press, Oxford, UK, 1988.
- [5] R.V. Pound, *Phys. Rev.* 81 (1951) 156.
- [6] E.M. Purcell, R.V. Pound, *Phys. Rev.* 81 (1951) 279.
- [7] A. Abragam, W.G. Proctor, *Phys. Rev.* 109 (1958) 1441.
- [8] A.G. Redfield, *Phys. Rev.* 98 (1955) 1787.
- [9] A.W. Overhauser, *Phys. Rev.* 92 (1953) 411.
- [10] T.R. Carver, C.P. Slichter, *Phys. Rev.* 92 (1953) 212.
- [11] I. Solomon, *Phys. Rev.* 99 (1955) 559.
- [12] I. Solomon, N. Bloembergen, *J. Chem. Phys.* 25 (1956) 261.
- [13] A. Abragam, J. Combrisson, I. Solomon, *C. r. hebd. séances Acad. sci.* 245 (1957) 157.
- [14] M-A. Bouchiat, T.R. Carver, C.M. Varnum, *Phys. Rev. Lett.* 5 (1960) 373.
- [15] F.D. Colegrove, L.D. Scheerer, G.K. Walters, *Phys. Rev.* 132 (1963) 2561.
- [16] T.R. Gentile, P.J. Nacher, B. Saam, T.T.G. Walker, *Rev. Mod. Phys.* 89 (2017) 045004.
- [17] A. Abragam, M. Goldman, *Rep. Prog. Phys.* 41 (1978) 395.
- [18] A. Abragam, M. Goldman, *Nuclear Magnetism: Order and Disorder*, Oxford University Press, Oxford, UK, 1982 (Chap. 6).
- [19] T. Wenckebach, *Essentials of Dynamic Nuclear Polarization*, Spindrift Publications, The Netherlands, 2016.
- [20] C.D. Jeffries, *Phys. Rev.* 106 (1957) 164.
- [21] A. Abragam, W.G. Proctor, *C. r. hebd. séances Acad. sci.* 246 (1958) 2253.
- [22] M. Goldman, A. Landesman, *C. r. hebd. séances Acad. sci.* 252 (1961) 263.
- [23] M. Goldman, in: J. Smidt (Ed.), *XIth Colloque Ampère on Magnetic and Electric Resonance and Relaxation*, Eindhoven, The Netherlands, July 1962, North Holland, Amsterdam, 1963, p. 688.
- [24] M. Goldman, A. Landesman, *Phys. Rev.* 132 (1963) 610.
- [25] I. Solomon, in: J. Smidt (Ed.), *XIth Colloque Ampère on Magnetic and Electric Resonance and Relaxation*, Eindhoven, The Netherlands, July 1962, North Holland, Amsterdam, 1963, p. 25.
- [26] S.F.J. Cox, V. Bouffard, M. Goldman, *J. Phys. C* 6 (1973) L100.
- [27] M. Goldman, S.F.J. Cox, V. Bouffard, *J. Phys. C* 7 (1974) 2940.
- [28] W. De Boer, M. Borghini, K. Morimoto, T.O. Niinikoski, *J. Low Temp. Phys.* 15 (1974) 249.
- [29] W. De Boer, *J. Low Temp. Phys.* 22 (1976) 185.
- [30] A. Abragam, M. Goldman, *Nuclear Magnetism: Order and Disorder*, Oxford University Press, Oxford, UK, 1982 (Chap. 8).
- [31] C. Urbina, J-F. Jacquinot, M. Goldman, *J. Phys. C* 19 (1986) 2275.
- [32] M. Goldman, J-F. Jacquinot, C. Urbina, *J. Phys. C* 19 (1986) 2299.
- [33] J-H. Ardenkjaer-Larsen, *J. Magn. Res.* 264 (2016) 3.