
A short introduction to Nuclear Magnetic Resonance

Pietro Carretta

Dipartimento di Fisica "A.Volta" and CNISM - University of Pavia - Via Bassi, 6 - 27100 Pavia (Italy)

The aim of this manuscript is to introduce some of the physical principles involved in nuclear magnetic resonance (NMR) spectroscopy, in order to allow a better understanding of the following parts of the book. The foundations of NMR have been settled decades ago [1] and its basic aspects are described in detail in several text books where also a complete formal derivation can be found. The reader can refer, for example, to the excellent monograph by C.P. Slichter [2] or to the book by A. Abragam [8] in order to unravel the physics underlying this spectroscopy. Although in some parts of this manuscript continuous wave (CW) NMR spectroscopy will be recalled we shall be dealing most of the time just with pulsed NMR technique.

1 Precessing moments and the rotating frame

A first issue to address is what is being measured by pulsed NMR technique. The answer to this question is not unique but still one can state on a rather general ground that by means of pulsed NMR one detects the time evolution of nuclear magnetization. Since the thermal energy $k_B T$ is in general much larger than the interaction among nuclear magnetic moments, in order to produce a non-zero magnetization one has to apply a magnetic field \mathbf{H}_0 . Accordingly a nuclear magnetization $M_0 = \gamma^2 \hbar^2 I(I+1)H_0/3k_B T$ arises, where I is the nuclear spin and γ its gyromagnetic ratio.

Let us first consider what is the effect of the magnetic field on the time evolution of a single magnetic moment \mathbf{M} . This simple problem can be solved within a classical approach and one finds that \mathbf{M} precesses around \mathbf{H}_0 (see Fig. 1) at the Larmor frequency $\omega_0 = \gamma H_0$. However, we are rather interested on the time-evolution of \mathbf{M} due to the interactions with the other degrees of freedom of our system (e.g. the electron spins, the other nuclear spins, the ionic charge distribution, etc...), not on the precessional motion around H_0 . Remember that actually \mathbf{H}_0 was applied just to generate a nuclear magnetization, as this is the quantity that will produce the NMR signal. Therefore it

may be convenient to study the time-evolution of the nuclear magnetization in a frame of reference, different from the laboratory one, where one can get rid of the effect of \mathbf{H}_0 on the time evolution of \mathbf{M} .

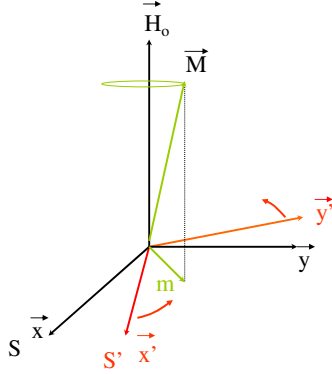


Fig. 1. Sketch of the precessional motion of a magnetic moment \mathbf{M} around \mathbf{H}_0 in the laboratory frame of reference S. The frame of reference S' rotating around \mathbf{H}_0 at a frequency ω is also shown. m is the component of \mathbf{M} in the xy plane.

This frame of reference is the one (S') rotating around \mathbf{H}_0 at a frequency $\omega \equiv \omega_0$ (see Fig. 1). In a frame of reference rotating at a frequency ω around \hat{z} , the magnetic moment is observed to precess around an effective field $\mathbf{H}_e = (H_0 - \omega/\gamma)\hat{z}'$. This effective field vanishes for $\omega = \omega_0$ so that \mathbf{M} no longer precesses in S'. Then any time-dependent perturbation at a frequency $\omega \rightarrow \omega_0$ (time-independent in S') would produce significant effects on the time-evolution of \mathbf{M} . For instance, let us consider the effect of a small RF field \mathbf{H}_1 rotating at frequency ω perpendicular to \mathbf{H}_0 , corresponding to a static field along \hat{x}' in S'. Then in S' the magnetic moment will precess around (see Fig. 2)

$$\mathbf{H}_e = (H_0 - \frac{\omega}{\gamma})\hat{z}' + H_1\hat{x}'$$

and for $\omega = \omega_0$ \mathbf{M} will precess just around \mathbf{H}_1 , at a frequency $\omega_1 = \gamma H_1$. Then one realizes it is convenient to analyze the time evolution of nuclear magnetization in a frame of reference rotating at ω_0 and, as we shall see later on, the detected NMR signal is indeed the one in the rotating frame S'.

For $\omega = \omega_0$ the RF field will drive \mathbf{M} away from the \hat{z} axes by an angle $\alpha(t)$ given by

$$\cos(\alpha(t)) = 1 - 2\sin^2\left(\frac{\omega_1 t}{2}\right). \quad (1)$$

Hence even a very small perturbation can drive the magnetization away from the \mathbf{H}_0 axes, provided that its frequency is very close ($\omega_1 \gg |\omega - \omega_0|$) to Larmor frequency. This is the classical description of the resonance process,

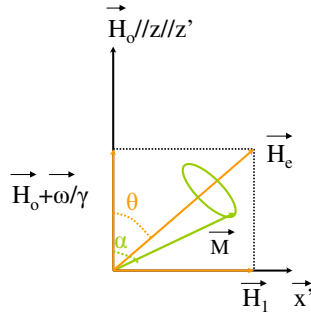


Fig. 2. Sketch of the time-evolution of \mathbf{M} in S' . The magnetic moment precesses around an effective field \mathbf{H}_e which for $\omega = \omega_0$ coincides with \mathbf{H}_1 . Notice that \mathbf{H}_0 and ω have opposite orientation.

which is the analogue of the resonance absorption driven by the magnetic-dipole transition mechanism, namely the one induced by the perturbation $\mathcal{H}_1(t) = -\gamma\hbar\mathbf{H}_1(t)$ of the Zeeman hamiltonian $\mathcal{H}_0 = -\gamma\hbar\mathbf{H}_0$. If, for simplicity, we refer to a spin $I = 1/2$ the energy level diagram is the one reported below where the notation $|2m_I\rangle$ for the eigenstates is used.

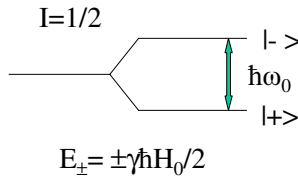


Fig. 3. Energy level diagram for a spin $I = 1/2$ in a magnetic field \mathbf{H}_0 and illustration of the transition induced by the RF field at frequency ω_0 .

One can estimate the expectation value

$$\langle I_z \rangle = (1/2)(p_+ - p_-),$$

with p_+ and p_- the probability to find the spin in state $|+\rangle$ and $|-\rangle$, respectively. Since $p_+ + p_- = 1$ one has

$$p_- = \frac{1 - 2\langle I_z \rangle}{2}$$

Then, if at $t = 0$ $p_+ = 1$ and $p_- = 0$ (i.e. $\mathbf{I} \parallel \mathbf{H}_0$), at time t (see Eq. 1 for comparison)

$$p_-(t) = \frac{1}{2}(1 - \cos\alpha(t)) = \sin^2\frac{\omega_1 t}{2}$$

for $\omega = \omega_0$. This equation corresponds to the well known Rabi equation giving the probability to pass from state $|+\rangle$ to state $|-\rangle$.

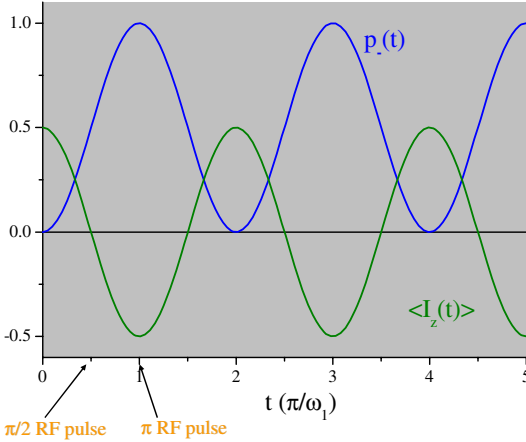


Fig. 4. Time evolution of $p_-(t)$ and of $\langle I_z \rangle$. It is pointed out that if the RF field is switched off after a time $\pi/2\omega_1$ $\langle I_z \rangle$ is zero, namely the spin expectation value has turned by $\pi/2$, from parallel to perpendicular to z . Then one says that a $\pi/2$ pulse was applied. In general, to turn by an angle θ $\langle I \rangle$ one has to apply an RF pulse of duration θ/ω_1 .

After a RF pulse (a $\pi/2$ pulse for example (see Fig. 4)) one can detect, with the same coil used to apply the RF, the voltage induced by the time evolution of nuclear magnetization. According to Faraday-Maxwell's law this voltage is proportional to the precessional frequency in the laboratory frame of reference S and to the nuclear in-plane magnetization $\langle M_{x,y}(t) \rangle$. The signal detected by the coil in S can be transformed into the one in S' by mixing it with a reference signal oscillating at ω_0 (e.g. $\cos(\omega_0 t)$). The low-frequency signal at the output of the mixer is the one detected in pulsed NMR experiments, the so-called FID (free induction decay) signal. The Bloch scheme of a typical pulsed NMR spectrometer is equivalent to the one of an MRI spectrometer (see Fig. 10 in the chapter by Lascialfari and Corti in this book), except for the pulsed gradient unit.

2 Time-evolution of nuclear magnetization and the Bloch equations

So far we have just considered the time evolution of a single spin. However, in general experiments are performed on a sample containing a statistical ensemble of nuclear spins and hence one has to consider how the statistical average of the spin components, namely the components of the nuclear magnetization, evolve in time. Then one can write for the statistical average

$$\langle \overline{I_{x,y,z}} \rangle = \sum_m \langle m | I_{x,y,z} | m \rangle \frac{e^{-E_m/k_B T}}{Z}$$

with $|m\rangle$ eigenstates of $\mathcal{H} = -\gamma\hbar I_z H_0$. For simplicity, if one considers an ensemble of nuclei with $I = 1/2$ in a magnetic field \mathbf{H}_0 one finds

$$\langle \overline{I_z} \rangle = \frac{1}{2} \frac{e^{-\gamma\hbar H_0/2k_B T} - e^{\gamma\hbar H_0/2k_B T}}{e^{-\gamma\hbar H_0/2k_B T} + e^{\gamma\hbar H_0/2k_B T}}$$

and

$$\langle \overline{I_{x,y}} \rangle = 0 .$$

Notice that for a single spin $\langle I_{x,y} \rangle$ is non-zero, while its average value is zero owing to the random phase of the x, y components of the spins. In general one can calculate the average statistical value starting from the density matrix $\rho = \exp(-\beta\mathcal{H})/Z$, with Z the partition function. Then

$$\langle \overline{I_z(t)} \rangle = Tr\{\rho(t)I_z\}$$

where the time evolution of $\rho(t)$ is given by

$$\frac{d\rho}{dt} = \frac{i}{\hbar} [\rho, \mathcal{H}]$$

Consider now the experimental configuration introduced in the previous section, where $\mathbf{H}_0 \parallel \hat{z}$ and the RF field \mathbf{H}_1 was perpendicular to it. Then $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1(t)$, where $\mathcal{H}_1 = -\gamma\hbar H_1 I_x$ can be treated as a perturbation of $\mathcal{H}_0 = -\gamma\hbar H_0 I_z$. Then one finds that

$$\langle \overline{M_y(t)} \rangle = M_0 \sin(\omega_1 t)$$

in the rotating frame. Again we observe that if the RF field is applied at a frequency ω_0 in S' $\langle \overline{M(t)} \rangle$ precesses just around \mathbf{H}_1 .

Although in certain cases it is rather simple to describe the time evolution of $\langle \overline{M_{x,y}(t)} \rangle$ in general, when one has to consider all hyperfine interactions present in a sample, this problem can become rather cumbersome. Therefore, it is convenient to consider the phenomenological equations devised by Bloch

[4] to describe the time evolution of the components of the nuclear magnetization in the lattice ¹:

$$\frac{dM_z}{dt} = \gamma(\mathbf{M} \times \mathbf{H}_0)_z + \frac{M_0 - M_z}{T_1}$$

$$\frac{dM_{x,y}}{dt} = \gamma(\mathbf{M} \times \mathbf{H}_0)_{x,y} - \frac{M_{x,y}}{T_2}$$

Here two characteristic decay times have been introduced: T_1 the spin-lattice relaxation time and T_2 the spin-spin relaxation time. T_1 describes the time evolution of M_z and is therefore directly related to the modifications in the population of the Zeeman levels, which can occur after the exchange of energy with the lattice excitations. The decay of $M_{x,y}$ occurs in a time T_2 , which is not only affected by the processes involved in the spin-lattice relaxation, but also by other processes which do not imply an exchange of energy with lattice excitations. For instance, as we shall see later on, the nuclear dipole-dipole interaction yields a spread in the resonance frequencies of the nuclei and accordingly a dephasing of the in-plane components of each nuclear moment takes place, yielding a decrease in $M_{x,y}$.

It is interesting to treat the resonance absorption starting from Bloch equations. Let us consider the effect of an RF field $H_1 \ll H_0$. Then one has to replace in the above equations \mathbf{H}_0 with

$$\mathbf{H} = H_1(\hat{x}\cos(\omega t) - \hat{y}\sin(\omega t)) + H_0\hat{z}$$

For a negligible RF field, namely $\gamma H_1 \ll 1/\sqrt{T_1 T_2}$, so that the magnetization

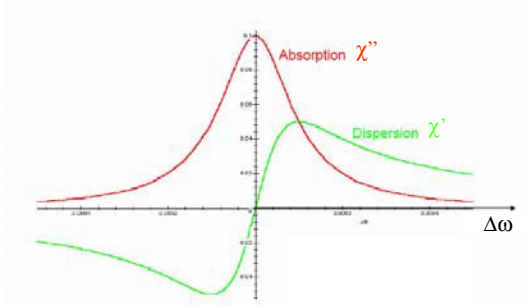


Fig. 5. Real ($\chi'(\omega)$) and imaginary ($\chi''(\omega)$) parts of the nuclear dynamical spin susceptibility.

is only slightly tilted from the z axes (i.e. $M_z \simeq M_0$), by considering solutions

¹ From now on we shall indicate the components of nuclear magnetization with $M_{x,y,z} = \langle \overline{M_{x,y,z}} \rangle$.

of the form $M_x = m\cos(\omega t + \phi)$ and $M_y = -m\sin(\omega t + \phi)$ one finds that the in-plane component of the magnetization (the one which can be detected with a coil in the xy plane)

$$m \simeq \frac{\omega_1 M_0 T_2}{\sqrt{1 + (\omega - \omega_0)^2 T_2^2}} .$$

If one derives the in-plane components of the magnetization oscillating in phase and out of phase by $\pi/2$ with the RF field, one can estimate the real and imaginary part of the nuclear spin susceptibility. One finds:

$$\chi'(\omega) = \frac{M_0}{H_0} \frac{\omega_0(\omega_0 - \omega)T_2^2}{1 + (\omega_0 - \omega)^2 T_2^2} ,$$

$$\chi''(\omega) = \frac{M_0}{H_0} \frac{\omega_0 T_2}{1 + (\omega_0 - \omega)^2 T_2^2} ,$$

the dissipative part of the nuclear spin susceptibility is a Lorentzian of width $1/T_2$ centered around ω_0 . In other words there is a peak in the absorption of the RF field at the Larmor frequency, which is spread over a certain width determined by the nuclear spin-spin relaxation time.

3 NMR spectra

When the sample under investigation is placed into the coil one observes a change in the inductance to

$$L = L_0[1 + 4\pi\chi(\omega)]$$

and a corresponding variation of the resistance by

$$\Delta R = L_0\omega 4\pi\chi'' .$$

Then one can estimate that the average power adsorbed by the nuclei

$$P(\omega) = \frac{1}{2}\omega H_1^2 \chi''(\omega)V ,$$

where V is the sample volume. For $\omega = \omega_0$, by recalling the expression derived for χ'' in the weak field limit, one would find

$$P(\omega_0) = \frac{1}{2}\omega_0^2 H_1^2 \chi_0 V T_2$$

So, one can derive directly $\chi''(\omega)$ from the power adsorbed by the circuit. Indeed, in CW NMR one directly detects $\chi''(\omega)$.

Since the spacing between adjacent hyperfine levels is not the same for all nuclei it is convenient to introduce a distribution function $f(\omega)d\omega$ giving the

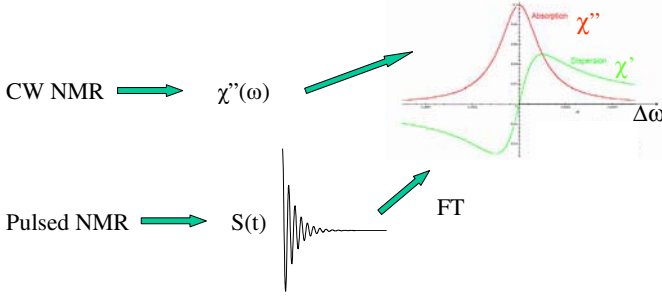


Fig. 6. Schematic illustration of the equivalence of the NMR spectra derived from CW NMR and from pulsed NMR spectroscopies after performing the Fourier transform (FT) of the FID signal.

fraction of nuclei with a resonance frequency between ω and $\omega + d\omega$. One can show that the energy adsorbed per unit time by the nuclei is

$$P(\omega) = \frac{\chi_0}{2} \omega \omega_0 H_1^2 f(\omega) 2\pi$$

If we now compare the above equation with the expression previously derived for $P(\omega)$ one finds that

$$\chi''(\omega) = 2\pi f(\omega) \omega_0 \chi_0$$

Then the signal detected in a CW NMR experiment, directly proportional to $P(\omega)$, is proportional to $\chi''(\omega)$ and gives the number of nuclei which are resonating with frequency between ω and $\omega + d\omega$, namely the NMR spectrum $f(\omega)$. On the other hand, by resorting to the fluctuation-dissipation theorem, one can show that

$$f(\omega) \propto \chi''(\omega) = \frac{\omega}{k_B T} \int_0^\infty e^{i\omega t} \langle \overline{M_x(t) M_x(0)} \rangle dt$$

namely, the NMR spectrum is the Fourier transform at frequency ω of the correlation function for the transverse components of the nuclear magnetization, proportional to the signal measured in the pulsed NMR experiment (see Fig. 6).

4 Moment expansion of the NMR signal

In order to establish a priori the shape of the NMR spectra or of the FID signal one has to consider all the interactions acting on the nuclei. The nuclear hyperfine hamiltonian can be written in the form

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{n-n} + \mathcal{H}_{n-e} + \mathcal{H}_{EFG}$$

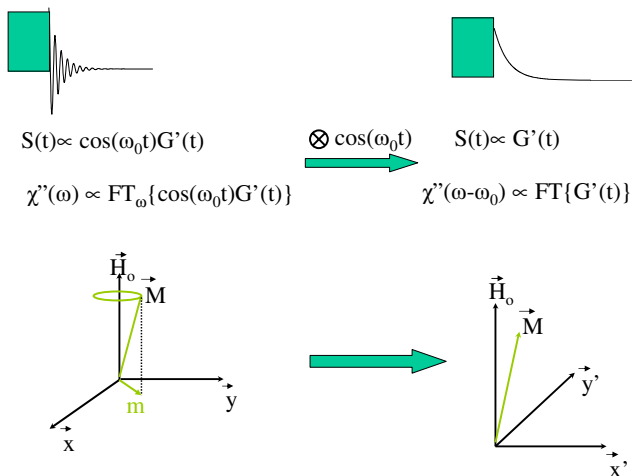


Fig. 7. Schematic view of the passage from the laboratory (left) to the frame of reference rotating at frequency ω_0 . At the top the effect on the FID signal after a $\pi/2$ pulse is shown. The signal detected in the laboratory frame is transformed into the one in the rotating frame by mixing it with a reference signal proportional to $\cos(\omega_0 t)$. Then the difference in the expressions for the FID signal $s(t)$ and NMR spectra are shown. Finally, at the bottom, the vectorial illustration of the magnetization in the two reference frames is shown.

where the first term is the Zeeman-like interaction with \mathbf{H}_0

$$\mathcal{H}_Z = -\gamma\hbar \sum_i I_z^i H_0 .$$

\mathcal{H}_{n-n} is nuclear dipole-dipole interaction, \mathcal{H}_{n-e} describes the interaction between the nuclear and electron spins, while \mathcal{H}_{EFG} is the quadrupole hamiltonian associated with the interaction of the nuclear quadrupole moment Q (non-zero for $I > 1/2$) with the electric field gradient (EFG) generated by the charge distribution around the nucleus.

Let us consider for simplicity just the first two terms of the hyperfine hamiltonian. Then

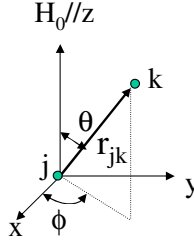
$$\mathcal{H} = -\gamma\hbar H_0 \sum_j I_z^j + \sum_{j < k} \frac{\hbar^2 \gamma^2}{r_{jk}^3} \left(\mathbf{I}^j \mathbf{I}^k - 3 \frac{(\mathbf{I}^j \mathbf{r}_{jk})(\mathbf{I}^k \mathbf{r}_{jk})}{r_{jk}^2} \right) .$$

It is convenient to write the nuclear dipole-dipole hamiltonian in the form

$$\mathcal{H}_{n-n} = \sum_{j < k} \frac{\hbar^2 \gamma^2}{r^3} \left(A + B + C + D + E + F \right)_{jk}$$

with

$$\begin{aligned}
A_{jk} &= I_z^j I_z^k f(\theta, \phi) \quad \Delta m_T = 0 \\
B_{jk} &= -(I_+^j I_-^k + I_-^j I_+^k) \frac{f(\theta, \phi)}{4} \quad \Delta m_T = 0 \\
C_{jk} &= (I_z^j I_+^k + I_+^j I_z^k) g(\theta, \phi) \quad \Delta m_T = 1 \\
D_{jk} &= C_{jk}^* \quad \Delta m_T = -1 \\
E_{jk} &= (I_+^j I_+^k + I_+^j I_+^k) h(\theta, \phi) \quad \Delta m_T = 2 \\
F_{jk} &= E_{jk}^* \quad \Delta m_T = -2
\end{aligned}$$



Since $\mathcal{H}_Z \gg \mathcal{H}_{n-n}$ only the terms of \mathcal{H}_{n-n} that commute with \mathcal{H}_Z will to the first order contribute to the time evolution of nuclear magnetization, namely the A and B terms. Then one has that the FID signal in the laboratory frame is given by

$$G(t) = \cos(\omega_0 t) \langle M'_x(t) M_x(0) \rangle$$

where

$$G'(t) = \langle M'_x(t) M_x(0) \rangle = \text{Tr} \{ e^{i\mathcal{H}'_{n-n} t/\hbar} M_x e^{-i\mathcal{H}'_{n-n} t/\hbar} M_x \}$$

with

$$\mathcal{H}'_{n-n} = \sum_{j < k} \frac{\hbar^2 \gamma^2}{r_{jk}^3} (A + B)_{jk}$$

In the frame of reference rotating at frequency ω_0 , the FID is directly given by $G'(t)$. Namely we have removed the term $\cos(\omega_0 t)$ which was just describing the precessional motion around \mathbf{H}_0 . Once more one realizes that if we work in the rotating frame we probe just the time-evolution of the nuclear magnetization due to the microscopic interactions within the sample.

For $\gamma^2 \hbar t / r^3 < 1$ one can write

$$G'(t) = G'(0) \left[\mathcal{M}_0 + \mathcal{M}_2 \frac{t^2}{2} + \mathcal{M}_4 \frac{t^4}{4!} + \dots \right],$$

where here \mathcal{M}_n represents the n^{th} moment of the NMR spectrum in the rotating frame ($\propto FT\{G'(t)\}$). The second moment, for example, is given by

$$\mathcal{M}_2 = -\frac{\text{Tr}\{[\mathcal{H}'_{n-n}, I_x]^2\}}{\text{Tr}\{I_x^2\}}$$

By writing \mathcal{H}'_{n-n} in polar coordinates one finds

$$\mathcal{M}_2 = \gamma^4 \hbar^2 \frac{I(I+1)}{3} \sum_k \left(\frac{3}{2} \frac{1 - 3\cos^2(\theta_k)}{r_k^3} \right)^2$$

Thus, one realizes that by deriving \mathcal{M}_2 from the FID signal one can estimate in a rather precise way the interatomic distances, for example.

If one considers the dipolar interaction with nuclei S of a different species one finds

$$\mathcal{M}_2 = \frac{4}{9} \gamma_I^2 \gamma_S^2 \hbar^2 \frac{S(S+1)}{3} \sum_{j < k} \left(\frac{3}{2} \frac{1 - 3\cos^2(\theta_{jk})}{r_{jk}^3} \right)^2$$

It has be remarked that nuclear spins can interact also through and indirect coupling mediated by electron spins, usually much weaker than the classical one described above, of the form

$$\mathcal{H}_{n-n}^{\text{ind}} = J \mathbf{I}_i \mathbf{I}_j$$

with J a scalar. This interaction is of major relevance in high resolution NMR spectroscopy and is responsible for the appearance of multiplets formed by $2(n-1)I+1$ lines, where n is the number of interacting nuclei of the same species. On the other hand, in certain cases, when the hyperfine coupling with electron spins is quite large, an indirect interaction (with J a tensor) larger than the direct one can be observed. Such a scenario occurs in the cuprates, for example [5].

5 Electron-nucleus hyperfine interaction

Let us now consider the interaction with the electron spins, which can often be written in the form

$$\mathcal{H}_{n-e} = -\gamma \hbar \sum_{i,k} \mathbf{I}_i \tilde{A}_{ik} \mathbf{S}_k$$

with \tilde{A}_{ik} the hyperfine coupling tensor. Then, there will be an hyperfine field at the i -th nucleus given by $\mathbf{h}_i = \sum_k \tilde{A}_{ik} \mathbf{S}_k$. If the electron spins have a non-zero average polarization $\langle \mathbf{S} \rangle$ then the local field probed by the nuclei will be $\mathbf{h}_i = \sum_k \tilde{A}_{ik} \langle \mathbf{S}_k \rangle$ and one can directly estimate $\langle \mathbf{S} \rangle$ from the

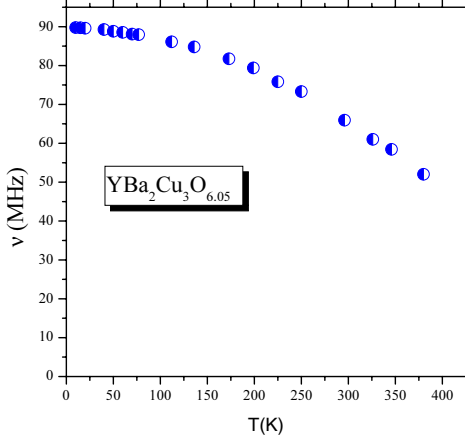


Fig. 8. Temperature dependence of ^{63}Cu $1/2 \rightarrow -1/2$ zero-field resonance frequency in the antiferromagnetic phase of $\text{YBa}_2\text{Cu}_3\text{O}_{6.05}$ vs. temperature. The resonance frequency is directly proportional to the order parameter, namely to the thermal average of Cu^{2+} spin $\langle \mathbf{S} \rangle$ [6].

resonance frequency in the local field. When an external field is applied the nuclei will experience a magnetic field

$$\mathbf{H} = \mathbf{H}_0 + \sum_k \tilde{A}_{ik} \langle \mathbf{S}_k \rangle$$

and the resonance frequency will be shifted to

$$\omega = \omega_0(1 + \Delta K)$$

with

$$\Delta K = \frac{\sum_k \tilde{A}_{ik} \langle \mathbf{S}_k \rangle}{H_0}.$$

Then one can write that $\Delta K = \sum_k \tilde{A}_{ik} \chi(\mathbf{q} = 0, \omega = 0)$ and one notices that from the shift of the NMR resonance spectrum one can derive the static uniform susceptibility associated with those electron spins which interact with the nuclear ones. Another contribution to the shift, usually smaller than the one involving the electron spins, arises from the screening of the magnetic field by the electrons on the ligands and by the core electrons. This shift depends significantly on the chemical bonding around the nuclei and for this reason is called chemical shift.

The electric quadrupole hamiltonian describing the interaction between the nucleus quadrupole moment Q and the EFG tensor \tilde{V} generated by the charge distribution around the nucleus is

$$\mathcal{H}_{EFG} = \sum_i \frac{e^2 Q V_{ZZ}}{4I(2I-1)} \left(3(I_z^i)^2 - I(I+1) + \frac{\eta}{2} [(I_+^i)^2 + (I_-^i)^2] \right)$$

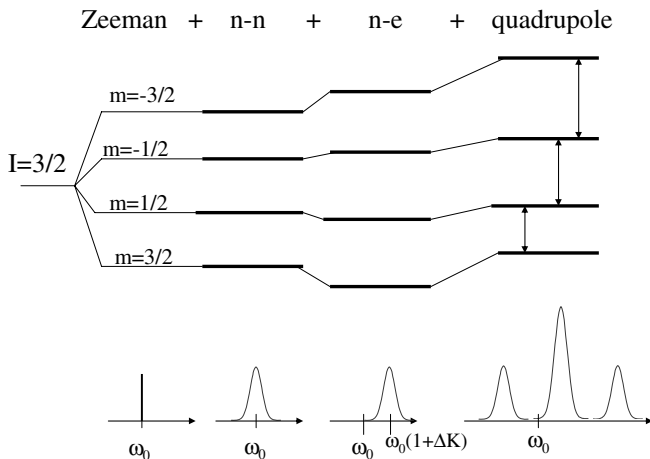


Fig. 9. Schematic illustration of the modifications in the hyperfine levels of $I = 3/2$ nuclei, due to the different terms of the nuclear hyperfine hamiltonian. The corresponding modifications in the NMR spectra are reported at the bottom of the figure.

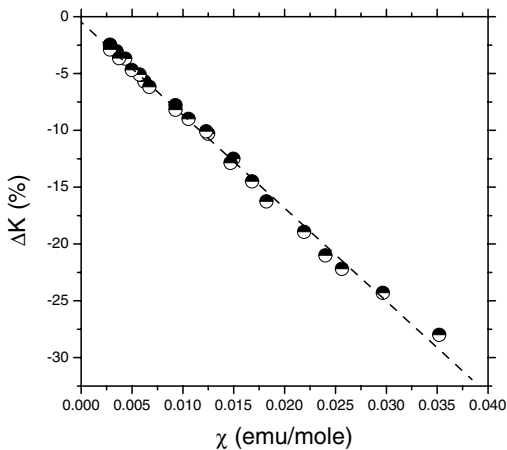


Fig. 10. The shift of ^{29}Si NMR frequency in MnSi is reported as a function of the macroscopic susceptibility measured with a SQUID magnetometer. The slope of the plot directly yields the hyperfine coupling, while the intercept gives the chemical shift (almost negligible here).

where V_{ZZ} is the main component of the EFG tensor written in the frame of reference of its principal axes (X, Y and Z)

$$\eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}} \quad \text{with } |V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$$

is the EFG tensor asymmetry parameter. If this is the only relevant hyperfine interaction the degeneracy between the spin components is partially resolved (Fig. 11) and one can induce transitions between the hyperfine levels by irradiating the nuclei at a frequency

$$\nu_Q = \frac{3eV_{ZZ}Q}{h2I(2I-1)} \left(1 + \frac{\eta^2}{3}\right)^{1/2}.$$

This resonance frequency is extremely sensitive to the symmetry of the charge distribution around the nuclei and hence to the presence of lattice distortions, as shown in Fig. 11.

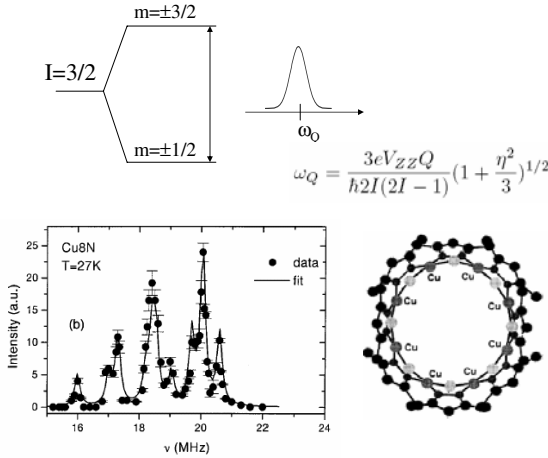


Fig. 11. At the top a schematic illustration of the transitions involved in an NQR experiment on $I = 3/2$ nuclei is presented. In the lower part of the figure $^{63,65}\text{Cu}$ ($I = 3/2$) NQR spectrum in Cu8 molecular ring is shown. It is evidenced that although in principle all Cu sites should be equivalent, a difference is present at the microscopic level, possibly associated with a lattice distortion [7].

When both Zeeman and quadrupole interactions are present the eigenvalues will depend on the orientation of the magnetic field with respect to the EFG principal axis. Then, in a powder sample there will be a distribution of possible orientations and of resonance frequencies. Therefore, the NMR powder spectra can become very broad if the quadrupole interaction is sizeable. The powder spectrum $f(\nu)$ can be estimated from the number of nuclei resonating at frequency ν which, for instance if $\eta = 0$, is simply given by

$f(\nu) \propto \sin(\theta(\nu))/(d\nu/d\theta)$ (θ is the polar angle defining the orientation of \mathbf{H}_0 with respect to Z in the XYZ frame of reference).

6 Effect of the motions on the NMR spectra

Due to the time dependence of the hyperfine hamiltonian one can observe a modification in the NMR spectra. Let us consider a rather standard situation where the rigid lattice NMR spectrum is a Gaussian and the local field at the nuclei is fluctuating. Then the FID signal is given by

$$G'(t) \propto Tr\{e^{i\mathcal{H}'_P t/\hbar} I_x e^{-i\mathcal{H}'_P t/\hbar} I_x\}$$

where $\mathcal{H}'_P(t)$ is the time-dependent hamiltonian which can be considered as a perturbation of the Zeeman hamiltonian. Suppose that the time-dependence is induced by fluctuations of the local field at the nucleus (for example due to molecular motions, spin fluctuations, ionic diffusion, flux lines lattice motion in a superconductor, etc...). Then one can write

$$\mathcal{H}'_P(t) = -\hbar \sum_i I_z^i \Delta\omega_i(t) = -\hbar\gamma \sum_i I_z^i h_z^i(t)$$

where $\Delta\omega_i(t)$ describes the fluctuations in the resonance frequency of the i -th nucleus. If we consider a stationary gaussian distribution for the fluctuations with a mean-square amplitude $\langle \Delta\omega^2 \rangle$, then one finds that

$$G'(t) = G'(0) \exp\left(-\langle \Delta\omega^2 \rangle \int_0^t (t-\tau)g(\tau)d\tau\right) \quad (2)$$

where $g(\tau) = \langle \Delta\omega(t+\tau)\Delta\omega(t) \rangle / \langle \Delta\omega^2 \rangle$ is the normalized correlation function describing the fluctuations of the resonance frequency.

Now one can introduce the corresponding correlation time

$$\tau_c = \int_0^\infty g(\tau)d\tau$$

which describes the characteristic decay time for $g(\tau)$. Without making any assumption on the analytical form of $g(\tau)$ one can distinguish two limiting cases:

a) Slow motions regime. The correlation time is extremely long and the FID is recorded over a time $t \ll \tau_c$. Then in Eq. 2 one can set $g(\tau) \simeq g(0) \simeq 1$, so that

$$G'(t) \simeq G'(0)e^{-\langle \Delta\omega^2 \rangle t^2/2}$$

namely a Gaussian decay, as it has to be expected since we have assumed a rigid lattice Gaussian spectrum with a second moment $\langle \Delta\omega^2 \rangle$.

b) Fast motions regime. The FID signal is recorded over a time $t \gg \tau_c$. Then one can set the upper limit of the integral in Eq. 2 to ∞ and neglect τ with respect to t , since $g(\tau)$ has already vanished over the time t . Then

$$G'(t) \simeq G'(0)e^{-\langle \Delta\omega^2 \rangle t \tau_c} = G(0)e^{-t/T_2'}$$

where

$$\frac{1}{T_2'} = \langle \Delta\omega^2 \rangle \tau_c = \gamma^2 \int_0^\infty \langle h_z(t)h_z(0) \rangle dt$$

is the relaxation rate of the FID signal, namely of the transverse magnetization. One observes that now the FID decay is exponential and thus the corresponding NMR spectrum is a lorentzian with full width at half maximum equal to $1/T_2'$. Upon decreasing τ_c the linewidth decreases and one observes the motional narrowing of the NMR line.

If $g(\tau) = \exp(-\tau/\tau_c)$ then one can write

$$G'(t) = G'(0)e^{-\langle \Delta\omega^2 \rangle \tau_c^2 [\exp(-t/\tau_c) - 1 + (t/\tau_c)]}$$

which nicely interpolates between fast and slow motions regime.

7 The spin echo

In general one observes that the decay of the FID signal is affected not only by intrinsic effects but also by extrinsic effects as magnetic field inhomogeneities associated, for example, with a distribution of paramagnetic shifts or simply to the inhomogeneity of the magnetic field generated by the magnet over the sample volume. Then one has an additional contribution to the decay of the FID, namely

$$G(t) = G(0)\exp(-t/T_2')\exp(-\gamma\Delta H t) = G(0)\exp(-t/T_2^*)$$

with ΔH the magnetic field distribution. Sometimes T_2^* can be so short that it is not even possible to record the FID signal. To avoid this problem one can resort to the **spin-echo** technique. Let us suppose that the magnetic field distribution is static and we apply the pulse sequence in Fig. 12.

The effect of the π RF pulse is to reverse the time evolution of the in-plane components of the nuclear spins. So, one observes that the dephasing of the spins during the first half of the sequence (between 0 and t) is recovered in the second half, after the π pulse, and the in-plane magnetization recovers at $2t$ and produces an echo signal. It is evident that the refocussing of the nuclear spins can occur as far as the resonance frequency of each nucleus during the first half and the second half of the pulse sequence is the same.

As an illustrative example let us consider what happens if the magnetic field is changed at time t , when the π RF pulse is applied. This is done, for example, in a controlled way in a spin-echo double resonance (SEDOR)

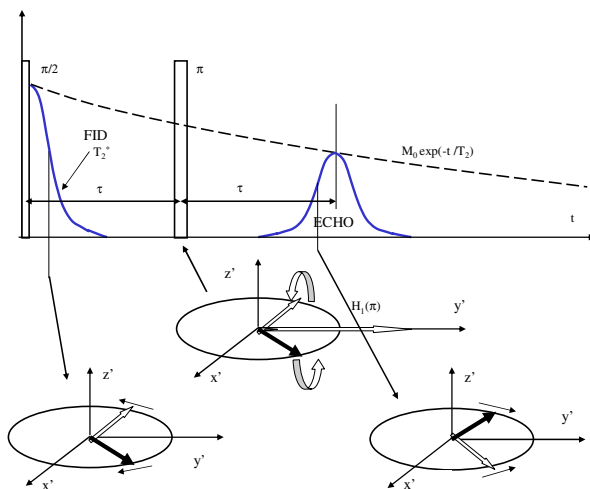


Fig. 12. Schematic representation of the motions of the nuclear spins generating the echo signal upon application of a sequence of $\pi/2$ and π RF pulses. It is shown how the FID signal after the $\pi/2$ pulse decays in a rather short time T_2^* owing to the dephasing of the nuclear spins. An echo is formed at time $2t$ thanks to the refocussing of the spins after the π RF pulse. The decay of the echo occurs over a time $T_2 \geq T_2^*$. It should be remarked that with pulse techniques, by switching the phase of the RF field it is possible to apply the second pulse (at time t) along a direction different from the one of the first pulse at $t = 0$ (e.g. from x to y in the rotating frame).

experiment, where at time t one applies a π pulse also on the nuclei S which are coupled to I nuclei through a $\mathcal{H}_{IS} = a\mathbf{I}\cdot\mathbf{S}$. The π pulse on S yields a change in the resonance frequency of the I nuclei during the second half. Accordingly a decrease in the echo signal of the I nuclei is detected and the coupling between the two nuclear species is estimated.

Let us now consider the more general situation where the magnetic field fluctuations are described by a gaussian stationary distribution function. If now one calculates the dephasing of the nuclear spins between the $\pi/2$ and π ($0 - t$) pulse and then between the π pulse and the echo ($t - 2t$) one derives that the echo amplitude at time $2t$ is given by

$$E(2t) = E(0)\exp\left(-\langle \Delta\omega^2 \rangle \left[2 \int_0^\infty (t - \tau)g(\tau)d\tau - \int_0^t \tau g(\tau)d\tau - \int_t^{2t} (2t - \tau)g(\tau)d\tau \right] \right) .$$

Without making any assumption on $g(\tau)$, in the fast motions regime ($\sqrt{\langle \Delta\omega^2 \rangle} \tau_c \ll 1$) one finds that

$$E(2t) = E(0)e^{-\langle \Delta\omega^2 \rangle \tau_c 2t} = E(0)e^{-2t/T_2'}$$

namely the echo decays with the same characteristic time of the FID. In the very slow motions regime, i.e. $\sqrt{\langle \Delta\omega^2 \rangle} \tau_c \gg 1$ the echo sequence allows to rephase completely the nuclear magnetization and then

$$E(2t) \rightarrow E(0) .$$

On the other hand, if $\sqrt{\langle \Delta\omega^2 \rangle} \tau_c \simeq 1$ one finds

$$E(2t) = E(0)e^{-\frac{\langle \Delta\omega^2 \rangle (2t)^3}{3\tau_c}}$$

If $g(\tau) = \exp(-\tau/\tau_c)$ one can derive an expression valid in any limit [8]

$$E(2t) = E(0)\exp\left(-\langle \Delta\omega^2 \rangle \tau_c [2t - \tau_c(1 - \exp(-t/\tau_c))(3 - \exp(-\tau/\tau_c))]\right)$$

One notices that if $\sqrt{\langle \Delta\omega^2 \rangle} \tau_c \simeq 1$ the decay of the echo amplitude can be quite fast. After a time $2t$ the echo would have decayed by a factor $\exp(-\langle \Delta\omega^2 \rangle (2t)^3/3\tau_c)$. What happens if during the time $2t$ we apply n π pulses separated by a shorter delay $2t'$, so that $2t \simeq 2nt'$ (see figure below)? Then, after every π pulse there will be a decay of the echo by a factor $\exp(-\langle \Delta\omega^2 \rangle (2t')^3/3\tau_c)$ and after n π pulses by

$$\exp\left(-\frac{\langle \Delta\omega^2 \rangle n(2t')^3}{3\tau_c}\right) \gg \exp\left(-\frac{\langle \Delta\omega^2 \rangle (2t)^3}{3\tau_c}\right)$$

Hence the effect of the motions on the decay of the echo amplitude is significantly reduced. This particular echo sequence was first introduced by Carr and Purcell [9].

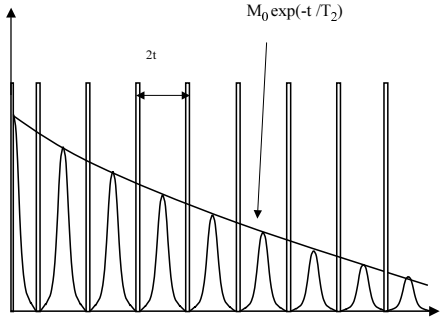


Fig. 13. Carr-Purcell sequence with Meiboom-Gill phase alternation. The π pulses are generated by an RF field which in S' is alternatively along $+x'$ and $-x'$.

8 Nuclear spin-lattice relaxation rate

As we have seen in Bloch equations the longitudinal component of nuclear magnetization relaxes back to its equilibrium value, determined by the temperature of the lattice, with a characteristic relaxation time T_1 . A simple RF pulse sequence which allows one to determine T_1 is shown in Fig. 14. After flipping the magnetization along x' with a $\pi/2$ pulse one waits for a delay τ and then applies a second $\pi/2$ pulse. The second $\pi/2$ will flip back along x' the fraction of magnetization which during the time τ has relaxed back to equilibrium. One can repeat the same experiment for different τ values and then derive T_1 .

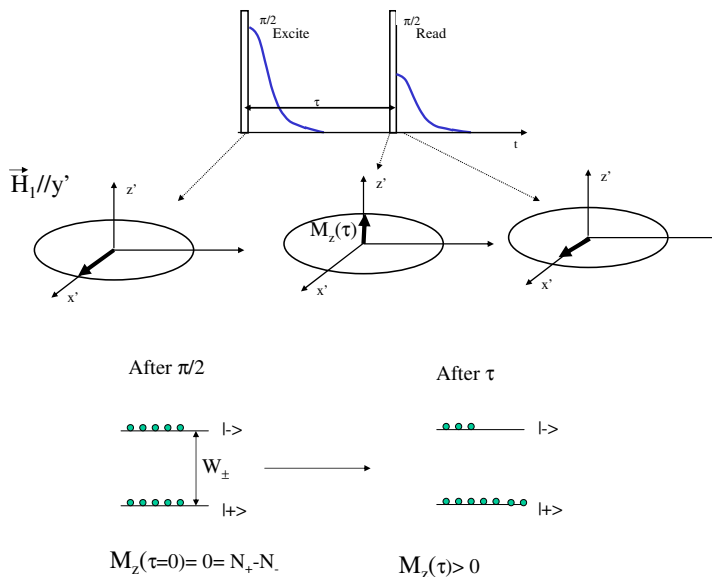


Fig. 14. (Top) Example of a simple RF pulse sequence used to measure the recovery of $M_z(\tau)$. The first $\pi/2$ turns the magnetization into the xy plane and the second pulse reads the amount of magnetization $M_z(\tau)$ which has relaxed back to equilibrium during the delay τ . The experiment is repeated for several values of τ to derive the recovery law of the magnetization. (Bottom) The effect of the first $\pi/2$ pulse on the statistical population on the hyperfine levels and its modification after τ are reported.

The recovery of nuclear magnetization towards equilibrium is determined by the transition probability among the hyperfine levels associated with the time-dependent part of the hamiltonian, namely by the lattice excitations.

The effect of the previous pulse sequence on the longitudinal magnetization can also be understood from the analysis of the statistical populations on the hyperfine levels (see Fig. 14). In fact, if we consider for simplicity nuclei with $I = 1/2$, then $M_z(\tau) \propto N_+ - N_-$, the difference of population between the two levels.

In general for nuclei with spin I one has $2I + 1$ states and one has to solve a system of $2I + 1$ differential equations

$$\frac{dN_m}{dt} = \sum_{n \neq m} (N_n W_{nm} - N_m W_{mn})$$

to derive the time evolution of the population difference between the levels which are being irradiated. For the simple case of $I = 1/2$ one finds that

$$M_z(\tau) = M_z(\tau \rightarrow \infty)(1 - e^{-\tau/T_1})$$

or equivalently

$$y(\tau) = \frac{M_z(\infty) - M_z(\tau)}{M_z(\infty)} = e^{-\tau/T_1}$$

with

$$\frac{1}{T_1} \equiv 2W_{\pm}$$

It should be noticed that in order to have spin-lattice relaxation $W_{\mp} > W_{\pm}$, but since usually $\hbar\omega_0 \ll k_B T$ $W_{\mp} \simeq W_{\pm}$ and one can express T_1 just in terms of one of the two transition probabilities. For $I > 1/2$ one has to consider all possible transitions which are driven by the time-dependent part of the hamiltonian. If the fluctuations are associated with an effective fluctuating magnetic field (e.g electron spin fluctuations) then just transitions with $\Delta m = \pm 1$ have to be considered in solving the system of differential equations. If the fluctuations are the ones of the electric field gradient, since \mathcal{H}_{EFG} is quadratic in the spin components, one has to consider also $\Delta m = \pm 2$ transitions. In general one finds a recovery law for nuclear magnetization

$$y(\tau) = \sum_j c_j e^{-\alpha_j \tau/T_1}$$

still with $1/T_1 = 2W_{\pm}^{I=1/2}$.

Let us suppose that the time-dependent part of the hamiltonian is associated with an effective magnetic field fluctuation

$$\mathcal{H}_P(t) = -\gamma \hbar \mathbf{I} \mathbf{h}(t)$$

which can be considered as a perturbation of the Zeeman hamiltonian. Then, starting from time-dependent perturbation theory one can express W_{\pm} in terms of the correlation function

$$g(\tau) = \langle \overline{\mathcal{H}_P(\tau)\mathcal{H}_P(0)} \rangle$$

describing the fluctuations of $\mathcal{H}_P(t)$. If $g(\tau)$ decays with a correlation time $\tau_c \ll T_1$ and $T_1\omega_0 \gg 1$, conditions which are usually satisfied, then one can write

$$\frac{1}{T_1} = \frac{\gamma^2}{2} \int_{-\infty}^{+\infty} e^{i\omega_0 t} \langle h_+(t)h_-(0) \rangle dt \quad (3)$$

This fundamental expression shows that $1/T_1$ is driven by the transverse components of the fluctuating field at the nucleus, to comply with magnetic-dipole selection rules, and that $1/T_1$ is proportional to the Fourier transform of the correlation function at the resonance frequency, to comply with energy conservation. In other terms $1/T_1$ probes the spectral density at ω_0 .

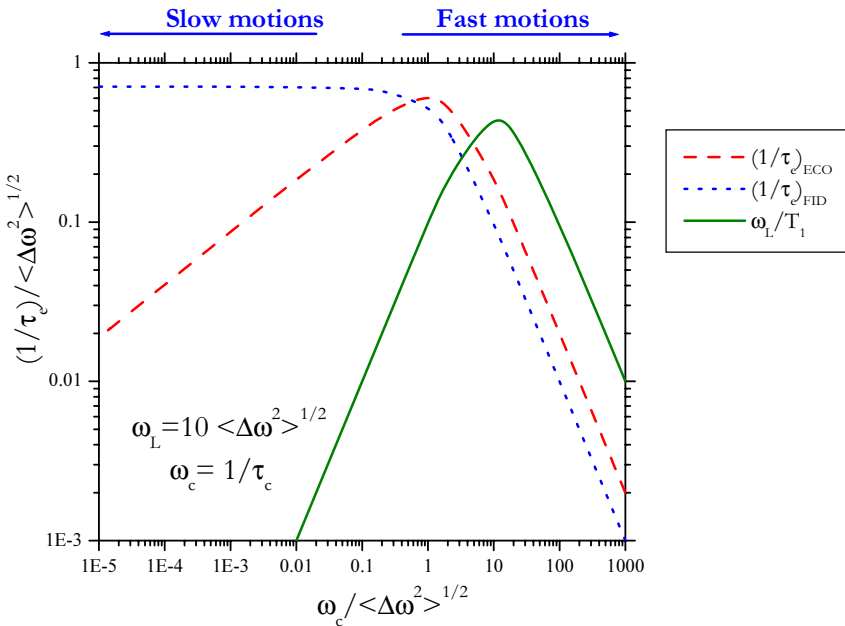


Fig. 15. Effect of the frequency of the fluctuations on the decay of the FID, of the echo and on $1/T_1$. $\langle \Delta\omega^2 \rangle$ is the second moment for the amplitude of the frequency fluctuations. τ_e is the characteristic time at which the FID or the echo decreases by a factor e . It has been assumed at the sake of illustration that the Larmor frequency is 10 times $\sqrt{\langle \Delta\omega^2 \rangle}$.

Suppose that $\langle h_+(t)h_-(0) \rangle = \langle \Delta h_{\perp}^2 \rangle \exp(-t/\tau_c)$. Then from Eq. 3 one derives that

$$\frac{1}{T_1} = \frac{\gamma^2}{2} \langle \Delta h_{\perp}^2 \rangle \frac{2\tau_c}{1 + \omega_0^2\tau_c^2} \quad (4)$$

One can distinguish three regimes:

a) Fast motions, $\omega_0\tau_c \ll 1$, then

$$\frac{1}{T_1} = \gamma^2 \langle \Delta h_{\perp}^2 \rangle \tau_c$$

Then one notices that if the fluctuations are isotropic so that $\langle \Delta h_{\perp}^2 \rangle = 2 \langle \Delta h_z^2 \rangle$ then if $\omega_0\tau_c \ll 1$ and $\sqrt{\langle \Delta \omega^2 \rangle} \tau_c \ll 1$ one finds $1/T_1 = 2/T_2'$.

b) Slow motions, $\omega_0\tau_c \gg 1$, then

$$\frac{1}{T_1} = \gamma^2 \langle \Delta h_{\perp}^2 \rangle \frac{1}{\omega_0^2 \tau_c}$$

c) $\omega_0\tau_c = 1$ then

$$\frac{1}{T_1} = \frac{\gamma^2}{2} \langle \Delta h_{\perp}^2 \rangle \frac{1}{\omega_0}$$

and one has a maximum in $1/T_1$, as it has to be expected since the highest transition probability would take place when the characteristic frequency for the fluctuations corresponds to the resonance frequency ω_0 .

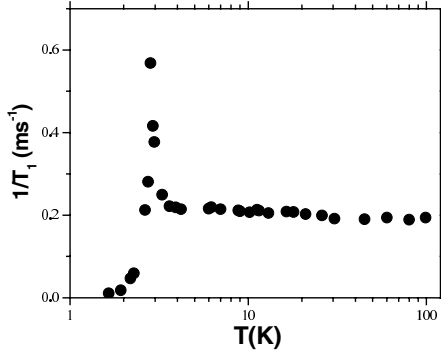


Fig. 16. Temperature dependence of ${}^7\text{Li}$ $1/T_1$ in $\text{Li}_2\text{VOSiO}_4$. It is evident that at temperatures larger than the exchange coupling ($\simeq 9$ K) the spin-lattice relaxation rate is temperature independent.

Let us now derive some typical expressions for nuclear spin-lattice relaxation rate which apply to some model systems. In a paramagnetic insulator the fluctuations are associated with electron spin fluctuations $\mathbf{h}(t) = \sum_i \tilde{A}_i \mathbf{S}_i(t)$. At high temperature, namely $k_B T \gg J$ (J the exchange coupling among the spins), the correlation function for the spin components is [10]

$$\langle S_{x,y,z}^i(t) S_{x,y,z}^i(0) \rangle = |S_{x,y,z}|^2 e^{-\omega_e^2 t^2 / 2}$$

with $\omega_e = (J/\hbar) \sqrt{2zS(S+1)/3}$ the Heisenberg exchange frequency. Then

$$\frac{1}{T_1} = \frac{\gamma^2}{2} \sum_i \left([A_{xx}^i]^2 + \dots \right) \frac{S(S+1)}{3} \frac{\sqrt{2\pi}}{\omega_e} ,$$

temperature independent. One notices that as $\omega_e \gg \omega_0$ (fast motions) $1/T_1 \propto 1/\omega_e$ and does not depend on ω_0 .

In general, when collective spin excitations are present one can write

$$\mathbf{h}(t) = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} \sum_i e^{i\mathbf{q}r_i} \tilde{A}_i \mathbf{S}_{\mathbf{q}}(t)$$

and by writing the transverse components of $\mathbf{h}(t)$ in $1/T_1$ expression one finds that

$$\frac{1}{T_1} = \frac{\gamma^2}{2} \frac{1}{N} \sum_{\mathbf{q}} \left(|A_{\mathbf{q}}|^2 S_{\alpha\alpha}(\mathbf{q}, \omega_0) \right)_{\perp} .$$

Here $|A_{\mathbf{q}}|^2$ is the form factor giving the hyperfine coupling of the nuclei with the spin excitations at wave-vector \mathbf{q} . $S_{\alpha\alpha}(\mathbf{q}, \omega_0)$ is the component of the dynamical structure factor at the resonance frequency. The term \perp indicates that one has to consider the products $|A_{\mathbf{q}}|^2 S_{\alpha\alpha}(\mathbf{q}, \omega_0)$ associated with the perpendicular components of the hyperfine field at the nucleus. From the fluctuation-dissipation theorem, by recalling that usually $k_B T \gg \hbar\omega_0$ one can also write

$$\frac{1}{T_1} = \frac{\gamma^2}{2} \frac{k_B T}{\hbar} \frac{1}{N} \sum_{\mathbf{q}} \left(|A_{\mathbf{q}}|^2 \chi''_{\alpha\alpha}(\mathbf{q}, \omega_0) \right)_{\perp}$$

One can now introduce the expressions for the dynamical susceptibility of a certain system and derive the corresponding expression of $1/T_1$. In a metal one finds

$$\frac{1}{T_1} = \left(\frac{16}{3} \right)^2 \pi^3 \hbar^2 \gamma^2 \mu_B^2 (|\psi(0)|^2)_{FS} D^2(E_F) k_B T .$$

where $D(E_F)$ is the density of states at Fermi level (E_F) and $|\psi(0)|^2$ is the probability that the electron is at the nuclear site. One observes that $1/T_1$ is linear in T , at variance with what was derived for a paramagnetic insulator. This is a simple evidence of Fermi-Dirac statistics, which tell us that, owing to Pauli principle, only a fraction $\simeq k_B T/E_F$ of all electron spins can flip and cause the relaxation.

In certain cases T_1 can be so short to prevent its direct measurement. However, under certain circumstances it still be possible to estimate it. Let us call S the spin of the fast relaxing nuclei and I the spin of another species of nuclei which one can suitably investigate. If S and I spins are coupled through nuclear dipole-dipole interaction, then the flip of spin S due to T_1^S processes is detected as a fluctuation of the local field at the I nuclear spin. Namely, one detects a dynamic with a correlation time $\tau_c = T_1^S$. This dynamic can manifest itself on the decay of the echo amplitude, for instance. If $\sqrt{\langle \Delta\omega_I^2 \rangle} T_1^S \ll 1$, where $\langle \Delta\omega_I^2 \rangle$ is the second moment of the frequency distribution associated

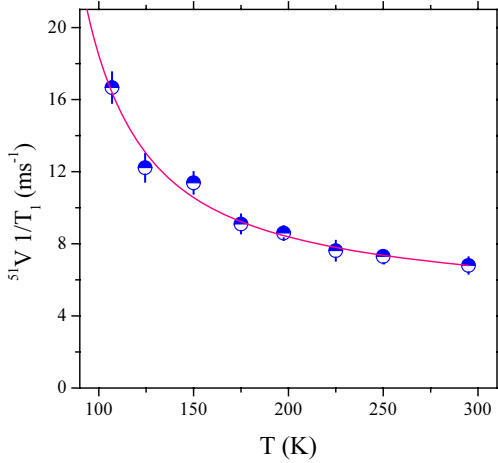


Fig. 17. Temperature dependence of $^{51}\text{V } 1/T_1$ in MoVO_5 estimated by measuring the decay rate of ^{95}Mo echo signal [11].

with the nuclear dipole interaction between S and I spins, then the decay of the echo amplitude of I spins is given by

$$E(2t) = E(0)e^{-\langle \Delta\omega_I^2 \rangle T_1^S 2t}$$

and then one can estimate T_1^S .

In pulsed NMR spectroscopy often one looks for the effect of the nuclear spins of a species S on the spins of another species I . This is the basis of the double resonance techniques, as the SEDOR one previously mentioned, of the Overhauser and cross-polarization techniques which allow to transfer polarization between different spin ensembles and of multi-dimensional techniques which are just a part of the marvellous realm of the nuclear magnetic resonance spectroscopy, which nowadays is employed in many different research areas [12].

References

1. E.M. Purcell, H.C. Torrey and R.V. Pound, Phys. Rev. 69, 37 (1946); F. Bloch, W.W. Hansen and M. Packard, Phys. Rev. 69, 127 (1946)
2. C. P. Slichter in *Principles of Magnetic Resonance* (Springer, Berlin, 1990) 3rd Ed.
3. A. Abragam in *Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961)
4. F. Bloch, Phys. Rev. 70, 460 (1946)

5. C. H. Pennington, D. J. Durand, C. P. Slichter, J. P. Rice, E. D. Bukowski and D. M. Ginsberg, Phys. Rev. B 39, 274 (1989)
6. C. Bucci, P. Carretta, R. De Renzi, G. Guidi, S. Jang, E. Rastelli, A. Tassi, and M. Varotto Phys. Rev. B 48, 16769-16774 (1993)
7. A. Lascialfari, Z. H. Jang, F. Borsa, D. Gatteschi, A. Cornia, D. Rovai, A. Caneschi, and P. Carretta Phys. Rev. B 61, 6839-6847 (2000)
8. M. Takigawa and G. Saito, J. Phys. Soc. 55, 1233 (1986)
9. H. Y. Carr and E. M. Purcell, Phys. Rev. 94, 630 (1954)
10. T. Moriya, Prog. Theor. Phys. 16, 23 (1956)
11. P. Carretta, N. Papinutto, C. B. Azzoni, M. C. Mozzati, E. Pavarini, S. Gonthier, and P. Millet Phys. Rev. B 66, 094420 (2002)
12. see for instance H. Friebolin in *Basic One- and Two-dimensional NMR Spectroscopy* (VCH, Weinheim, 1993) and <http://www.cis.rit.edu/htbooks/nmr/>.