

# Measuring the magnetic moment of the nucleus

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## 1 Theoretical background

Nuclear magnetic resonance (NMR) and electron spin resonance (ESR) have much common in their theoretical description as well as experimental methodology. So in the following we summarize the basic theoretical concepts concerning resonance absorption by magnetic moments, that are valid for both types of phenomena.

### 1.1 Magnetic moment and angular momentum

Consider a particle (electron, nucleon, nucleus, or even an atom or molecule) whose total angular momentum,  $\hat{\mathbf{J}}$ , and magnetic moment  $\hat{\boldsymbol{\mu}}$  are proportional to each other:

$$\boldsymbol{\mu} = \gamma \cdot \mathbf{J} \quad \Leftrightarrow \quad \hat{\boldsymbol{\mu}} = \gamma \cdot \hat{\mathbf{J}}.$$

This relation holds for the classical quantities as well as the quantum mechanical operators. Here  $\gamma$  is the so-called *gyromagnetic ratio*, its value is different for different systems.

The magnitude of  $\gamma$  can be estimated in a simple way. A classical, point-like particle with mass  $m$  and charge  $q$ , which moves with velocity  $v$  on a circular orbit of radius  $r$ , has  $J = mvr$  angular momentum, and generates a magnetic moment: for a current loop (almost by definition)  $\mu = I \cdot A$ , where  $I$  is the current and  $A$  is the area, so we have

$$\mu = I \cdot A = qv \frac{1}{2\pi r} \cdot r^2 \pi = \frac{qvr}{2}, \quad J = mvr \quad \Rightarrow \quad \mu = \frac{q}{2m} J.$$

So for a particle that moves classically

$$\gamma = \frac{q}{2m}. \tag{1}$$

This is valid also if we have multiple particles with the same charge to mass ratio.

Quantum mechanical (not necessarily elementary) particles have intrinsic angular momentum (spin), which does not stem from classical motion. It is usually measured in units of  $\hbar$ ; it is worthwhile to introduce the dimensionless  $j$  angular momentum quantum number:  $J = \hbar j$ . For such particles the above (1) relation is not true, but it gives a useful hint at the magnitude of the magnetic moment.

The electron is a particle with spin one-half, ie. its angular momentum is  $J_e = \hbar/2$  (or  $j = 1/2$ ), and its magnetic moment is, according to experiment

$$\mu_e = g_e \frac{e}{2m_e} J_e = g_e \frac{e}{2m_e} \frac{\hbar}{2} \equiv g_e \mu_B j, \quad \text{where} \quad \mu_B \equiv \frac{e\hbar}{2m_e} \approx 9.27 \cdot 10^{-24} \text{ J/T}. \quad (2)$$

For nucleons and nuclei

$$\mu = g \frac{e}{2m_p} J = g \frac{e\hbar}{2m_p} j \equiv g \mu_N j, \quad \text{where} \quad \mu_N \equiv \frac{e\hbar}{2m_p} \approx 5.05 \cdot 10^{-27} \text{ J/T}. \quad (3)$$

Here  $\mu_B$  is called *Bohr magneton*, and  $\mu_N$  is the *nuclear magneton*.  $g$  is simply called the  $g$  factor (sometimes it is called the gyromagnetic ratio). From the Dirac equation (the relativistic wave equation of particles with spin one half) one obtains  $g = 2$ . For electrons,  $g_e \approx 2.002322$ , the fact that this is not exactly 2 can be explained in quantum field theory. For protons, measurement tells that  $g_p \approx 5.585486$ , for neutrons,  $g_n \approx -3.826085$ ; although on the order of 1, so (1) was a good estimate, these are way different from 2. This hints at the composite nature of the nucleons (nowadays we know that they consist of quarks). For nuclei, the  $g$  factor can take a variety of different values.

## 1.2 Magnetic moment in external field

It is well known that a particle with angular momentum (spin)  $J = \hbar j$  has  $2j + 1$  possible quantum states, corresponding to the eigenvalues of the projection of the angular momentum in a given direction. Based on rotational symmetry we can assume that in the absence of external fields the energy levels of the system are degenerate with respect to these eigenvalues. If a static  $\mathbf{B}_0$  external magnetic field is applied, this degeneration vanishes, the levels split. If for simplicity we take the  $z$  axis in the direction of  $\mathbf{B}_0$ , we have for the interaction Hamiltonian

$$\hat{K} = -\hat{\boldsymbol{\mu}}\mathbf{B}_0 = -\gamma\hat{\mathbf{J}}\mathbf{B}_0 \equiv -\gamma B_0 \hat{J}_z.$$

The eigenstates of  $\hat{J}_z$  are characterized by the magnetic quantum number  $m$ , the effect of  $\hat{K}$  on these states is simple:

$$\hat{J}_z |m\rangle = m\hbar |m\rangle, \quad \hat{K} |m\rangle = E_m |m\rangle, \quad \text{where} \quad E_m = -\gamma\hbar B_0 m.$$

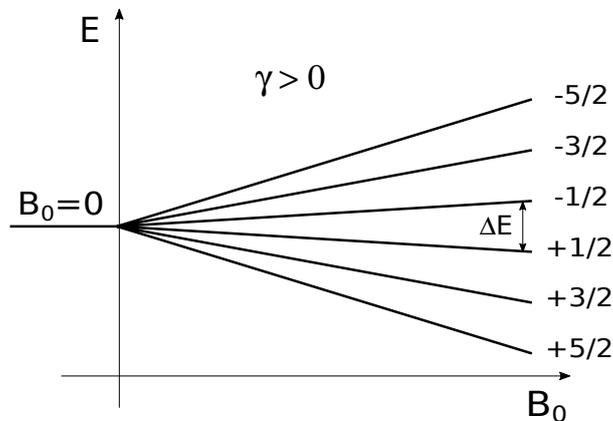


Figure 1: An energy level that is sixfold degenerate in the absence of external magnetic field splits if one applies the external field.

The energy difference between the neighboring levels is  $\Delta E = |\gamma| \hbar B_0$ . (There are cases (eg. the neutron) where  $\gamma < 0$ .) As an example, on Fig. 1.2 we see the energy levels as a function of the magnetic field for a particle with spin  $j = 5/2$ . If we are to measure the magnetic moment of the system (or the  $\gamma$  gyromagnetic ratio), we may want to measure  $\Delta E$  in a given magnetic field.

If in addition to  $\mathbf{B}_0$ , a time-dependent  $\mathbf{B}_1(t)$  magnetic field is present, it can cause transitions between some levels. For a harmonic perturbation the correction to the Hamiltonian is

$$\hat{H}'(t) = -\hat{\boldsymbol{\mu}}\mathbf{B}_1(t) = -\hat{\boldsymbol{\mu}}\mathbf{B}_1 \cos(\omega t) \equiv \hat{V} \cos(\omega t), \quad \text{where } \hat{V} = -\hat{\boldsymbol{\mu}}\mathbf{B}_1.$$

It is known that the transition probability  $W$  for unit time (in first-order perturbation theory) is

$$W_{m \rightarrow m'} = \frac{2\pi}{\hbar} \left| \langle m | \hat{V} | m' \rangle \right|^2 \delta(E_{m'} - E_m - \hbar\omega). \quad (4)$$

Now remember that according to the theory of angular momentum, the step operators  $\hat{J}_\pm$ , which change the  $m$  quantum number by  $\pm 1$ , are  $\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y$ . So the operators  $\hat{J}_x$  and  $\hat{J}_y$  transform the  $|m\rangle$  state in a superposition of  $|m+1\rangle$  and  $|m-1\rangle$ , while  $\hat{J}_z$  leaves  $m$  unchanged. So from Eq. (4) we conclude that only the component of  $\mathbf{B}_1$  that is perpendicular to  $\mathbf{B}_0$  causes transitions between states with different  $m$  (we took the  $z$  axis in the direction of  $\mathbf{B}_0$ ), and transitions can happen only between levels with  $m$  quantum numbers next to each other:  $m \rightarrow m' = m \pm 1$ . (This is only true for first order perturbation theory.) Energy conservation is assured by the Dirac delta, from which we get the following *resonance condition*:

$$\hbar\omega = \Delta E = |\gamma| \hbar B_0 \quad \Leftrightarrow \quad \omega = |\gamma| B_0.$$

Note that in the expression of  $\omega$  the Planck constant cancels. This usually occurs for quantum mechanical relations that can be arrived at with classical reasoning; this is such a case, as we will see soon.

### 1.3 Classical motion of magnetic moment

From the quantum mechanical treatment above we got  $\omega = |\gamma| B_0$ ; to better understand this, we briefly summarize the classical picture of the interaction of a magnetic field of the type seen above and a particle with magnetic moment (and angular momentum).

#### 1.3.1 Equation of motion, static field

In classical mechanics an external  $\mathbf{B}$  field exerts a torque  $\mathbf{M} = \boldsymbol{\mu} \times \mathbf{B}$  on a magnetic moment. For the angular momentum of a particle with gyromagnetic ratio  $\gamma$ , we can thus write up the equation of motion as

$$\frac{d\mathbf{J}}{dt} = \boldsymbol{\mu} \times \mathbf{B} \quad \Rightarrow \quad \frac{d\boldsymbol{\mu}}{dt} = \boldsymbol{\mu} \times (\gamma\mathbf{B}). \quad (5)$$

It is important to note that this equation is valid for any time-dependent  $\mathbf{B}(t)$  field. Note also that by taking the scalar product with  $\boldsymbol{\mu}$ , one readily sees that the magnitude of  $\boldsymbol{\mu}$  does not change, even in the case of time-dependent  $\mathbf{B}(t)$ . (We have reasoned classically; one would be very much surprised if  $\boldsymbol{\mu}$  would change its magnitude; this is impossible in a quantum mechanical setting.)

For solving Eq. (5), it is convenient to change the reference frame to a rotating one. As known from classical mechanics, the time-derivative of a vector  $\mathbf{A}(t)$  in the stationary laboratory frame,  $\frac{d\mathbf{A}(t)}{dt}$ , and the time-derivative of it taken in a reference frame rotating with a constant  $\boldsymbol{\Omega}$  angular velocity,  $\left. \frac{\delta\mathbf{A}(t)}{\delta t} \right|_{\boldsymbol{\Omega}}$ , are related by

$$\frac{d\mathbf{A}}{dt} = \left. \frac{\delta\mathbf{A}}{\delta t} \right|_{\boldsymbol{\Omega}} + \boldsymbol{\Omega} \times \mathbf{A}. \quad (6)$$

So in the rotating frame we have for the magnetic moment

$$\frac{d\boldsymbol{\mu}}{dt} = \boldsymbol{\mu} \times (\gamma\mathbf{B}) \quad \Rightarrow \quad \left. \frac{\delta\boldsymbol{\mu}}{\delta t} \right|_{\boldsymbol{\Omega}} = \boldsymbol{\mu} \times (\gamma\mathbf{B} + \boldsymbol{\Omega}) \equiv \boldsymbol{\mu} \times \mathbf{B}'_{\text{eff}}, \quad \text{where} \quad \mathbf{B}'_{\text{eff}} = \mathbf{B}' + \frac{\boldsymbol{\Omega}}{\gamma}.$$

This equation resembles to the one valid in the stationary frame, the difference is that instead of the  $\mathbf{B}$  field here we have an „effective field”  $\mathbf{B}'_{\text{eff}} = \mathbf{B}' + \frac{\boldsymbol{\Omega}}{\gamma}$ , that is the sum of the original  $\mathbf{B}$  field (with components written up in the rotating frame, hence the notation  $\mathbf{B}'$ ) and of a „virtual field”  $\boldsymbol{\Omega}/\gamma$ .

Any give physical process can be described in any reference frame; we can always choose one that makes the treatment simpler. For static  $\mathbf{B}(t) = \mathbf{B}_0$  field, it is useful

to take  $\boldsymbol{\Omega} = -\gamma\mathbf{B}_0$ , so that the effective field,  $\mathbf{B}'_{\text{eff}}$  becomes zero. Thus in the rotating frame  $\boldsymbol{\mu}$  is constant. It follows that in the laboratory frame, in a static  $\mathbf{B}_0$  field, the magnetic moment rotates (precesses) around the direction of the  $\mathbf{B}_0 = \mathbf{B}'_0$  field with an angular velocity

$$|\omega| \equiv \omega_L = \gamma B_0. \quad (7)$$

This  $\omega_L$  frequency is called the *Larmor frequency* of the spin in the  $\mathbf{B}_0$  field. Note that during the precession, the angle between the  $\boldsymbol{\mu}$  magnetic moment and the  $\mathbf{B}_0$  field does not change, so the energy stored by the momentum,  $-\boldsymbol{\mu}\mathbf{B}_0$  also remains constant.

### 1.3.2 Effect of a magnetic field with harmonic time dependence

We saw in the quantum mechanical treatment above that the addition of a small harmonic  $\mathbf{B}_1(t) = \mathbf{B}_1 \cos(\omega t)$  field that is perpendicular to the static  $\mathbf{B}_0$  field induces transitions between different eigenstates. Let's see what can be said about this situation classically.

For simplicity let's take the  $z$  axis again in the direction of  $\mathbf{B}_0$ , and let the  $x$  axis point in the direction of  $\mathbf{B}_1$ . We saw that rotating fields are easier to handle, so we consider the  $\mathbf{B}_1(t)$  field that has linear polarization in the  $x$  direction as a sum of two fields with opposite circular polarization in the  $x$ - $y$  plane:

$$\mathbf{B}_1(t) = \begin{pmatrix} B_1 \cos(\omega t) \\ 0 \\ 0 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} B_1 \cos(\omega t) \\ B_1 \sin(\omega t) \\ 0 \end{pmatrix} + \frac{1}{2} \begin{pmatrix} B_1 \cos(\omega t) \\ -B_1 \sin(\omega t) \\ 0 \end{pmatrix}.$$

We will see that out of these two circularly polarized components, only the one rotating in the direction of the precession of the magnetic moment in the  $\mathbf{B}_0$  field will have any significance, the effect of the other component will be non-important. So eventually we investigate the effect of a circularly polarized

$$B_{1x}(t) = B_1 \cos(\omega t), \quad B_{1y}(t) = B_1 \sin(\omega t), \quad B_{1z}(t) = 0$$

field. According to the considerations above, let's change to a rotating  $K'$  frame where the time dependence (rotation) of  $\mathbf{B}_1(t)$  cancels. So let the angular velocity seen in Eq. (6) be  $\Omega = \omega!$  In this reference frame,  $\mathbf{B}_0 = \mathbf{B}'_0$  and  $\mathbf{B}'_1$  are both static fields (let's take the zero point of time such that in the rotating frame  $\mathbf{B}'_1$  points in the  $x'$  direction), but we will have a virtual magnetic field with magnitude  $\omega/\gamma$  pointing in the  $z$  direction:

$$\left. \frac{\delta \boldsymbol{\mu}}{\delta t} \right|_{\omega} = \boldsymbol{\mu} \times \mathbf{B}'_{\text{eff}}, \quad \text{where} \quad \mathbf{B}'_{\text{eff}} = \begin{pmatrix} B_1 \\ 0 \\ B_0 + \omega/\gamma \end{pmatrix}.$$

On the left panel of Fig. 1.3.2 we see the effective field in the rotating frame. In this frame the motion of  $\boldsymbol{\mu}$  is basically a precession around  $\mathbf{B}'_{\text{eff}}$ , as seen in the middle panel

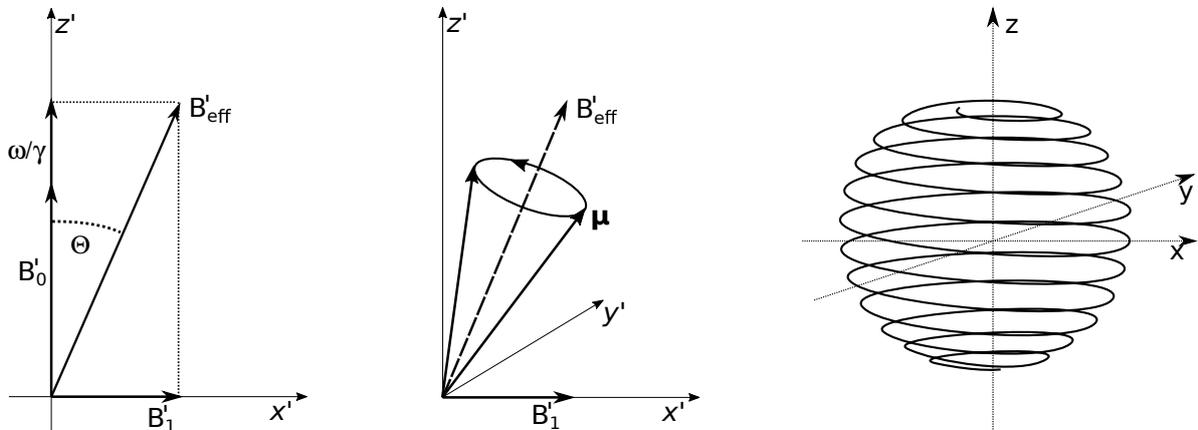


Figure 2: Left panel: The effective magnetic field and its components in the rotating frame, for a harmonic circular perturbing field. Middle panel: The precession of the magnetic moment around the effective field in the rotating frame. Right panel: The trajectory of  $\boldsymbol{\mu}$  in the case of resonance, seen from the stationary (laboratory) frame.

on the same figure. If initially the momentum points in the  $\mathbf{B}_0$  direction (ie. in the  $z$  direction), then after switching on  $\mathbf{B}_1$ , the angle between the magnetic moment and the  $\mathbf{B}_0$  field will periodically change between 0 and  $2\Theta$ , where

$$\text{tg}\Theta = \frac{B_1}{B_0 + \omega/\gamma}.$$

Because we assumed  $B_1 \ll B_0$ , the change in the angle (ie.  $\Theta$ ) will always be small, except if  $\omega$  is close to the Larmor frequency  $\omega_L = -\gamma B_0$ . In the  $\omega = \omega_L = -\gamma B_0$  case  $\mathbf{B}_{\text{eff}} = \mathbf{B}'_1$ , so in the rotating frame the moment precesses around  $\mathbf{B}'_1$ , in a way that its direction will change from that of  $\mathbf{B}_0$  to the opposite of it and back in every period. Since  $B_1 \ll B_0$ , this precession is much slower than the rotation of  $\mathbf{B}_1$ . So in the laboratory frame the motion of the magnetic moment can be visualized as a fast rotation around the  $\mathbf{B}_0$  field, during which the angle between  $\boldsymbol{\mu}$  and  $\mathbf{B}_0$  slowly changes between  $0^\circ$  and  $180^\circ$  között. We can see an illustration of this in the right panel of Fig. 1.3.2.

We see that the  $|\omega| = \gamma B_0$  frequency has a distinct role in the classical picture as well: if we superpose an external harmonic field with this frequency to the static  $\mathbf{B}_0$  field, then the energy stored in the magnetic moment by the  $\mathbf{B}_0$  field changes between its extremes,  $\mu B_0$  and  $-\mu B_0$ . The quantum mechanical argument based on perturbation theory suggested that for this frequency, we get transitions between the different states. The question is now how to measure this frequency — soon to be understood as and to be called *resonance frequency* — in a given  $B_0$  static external field; if this is accomplished, we can gain information on the  $\gamma$  gyromagnetic ratio.

## 2 Measurement of the resonance frequency

The bigger the static field  $B_0$ , the bigger the  $\omega_L$  resonance frequency, and as we will see, the more accurate measurement is possible. Under realistic conditions, one uses magnetic fields of at most a few teslas (T). In case of electron spin ( $\mu_e \approx \mu_B$ ), in a  $B_0 = 1$  T field, the resonance frequency is approx.  $1.4 \cdot 10^{10}$  Hz (this corresponds to a microwave with  $\lambda = 2.1$  cm wavelength), in case of nuclei, the  $\mu_N$  nuclear magneton sets the scale; for example, for protons, using  $g_p$  as given in Eq. (3), for  $B_0 = 1$  T the resonance frequency is approx. 42 MHz, so in this case we are in the realm of radio frequency signals.

The search for the  $\omega_L$  resonance frequency can be done in two ways: either the frequency of the excitation field is constant, and we change the magnitude of the  $B_0$  field, or the other way around. For nuclear magnetic moments both methods can be used, for electrons, practically only the first one, because for a given accuracy it is much more cumbersome to tune the frequency of microwaves than to set the magnetic field.

For the observation of resonance (that is, to detect when the applied  $\omega$  frequency exactly matches the  $\omega_L$  Larmor frequency) we have a handful of available methods:

- For free particles, if they are inserted in an inhomogeneous magnetic field, the change in the direction of their magnetic moment causes a shift in their trajectory (this is the Rabi molecular beam method).
- In condensed samples, the energy absorption from the external field that occurs in the case of resonance can be detected. In the following we go into the details about this, and we use this method in the laboratory course as well.
- One can detect the oscillating magnetic field generated by the magnetic moments that precess in a coherent way (Section 1.3.2). This is the principle of the so-called spin echo experiments; we briefly review this method at the end of this section.

### 2.1 Energy absorption in condensed matter, spin relaxation

Up to now we considered only spins (magnetic moments) as insulated objects. In any realistic setting, they interact with the surrounding medium. For simplicity, in the following we investigate particles with  $j = 1/2$  spin and  $g\mu_0 j = \frac{1}{2}g\mu_0$  magnetic moment. (For nuclei  $\mu_0 = \mu_N$ , for electrons  $\mu_0 = \mu_B$ ).

In a static  $B_0$  field there are two states of such a spin, the  $|m = +1/2\rangle \equiv |\uparrow\rangle$ , and the  $|m = -1/2\rangle \equiv |\downarrow\rangle$  state, with energies  $E_\uparrow = -\frac{1}{2}g\mu_0 B_0$ , and  $E_\downarrow = \frac{1}{2}g\mu_0 B_0$ , respectively. The total  $N_0$  number of spins is constant; let us denote the occupation numbers of these states (as a function of time) by  $N_\uparrow(t)$  and  $N_\downarrow(t)$ , and their difference by  $n(t)$ :

$$N_0 = N_\uparrow(t) + N_\downarrow(t) = \text{const}, \quad n(t) \equiv N_\uparrow(t) - N_\downarrow(t).$$

In thermodynamic equilibrium  $n(t) \equiv n_T$  is constant, and  $n_T > 0$ , since the lower energy states are more probable. For temperature  $T$ , using the canonical ensemble, with a little rearrangement we get

$$N_{\uparrow T} = A \exp\left(\frac{g\mu_0 B_0}{2k_B T}\right), \quad N_{\downarrow T} = A \exp\left(-\frac{g\mu_0 B_0}{2k_B T}\right) \quad \Rightarrow \quad n_T = N_0 \tanh\left(\frac{g\mu_0 B_0}{2k_B T}\right).$$

At room temperature the value of  $k_B T$  is approximately 0.024 eV. In a  $B_0 = 1$  T field, for nuclei the characteristic value of  $g\mu_N B_0$  is about  $2 \cdot 10^{-26}$  J ( $1.3 \cdot 10^{-7}$  eV), for electrons,  $\mu_B B_0$  is approx.  $10^{-23}$  J ( $6.2 \cdot 10^{-5}$  eV). We can conclude that the difference ( $n_T = N_{\uparrow T} - N_{\downarrow T}$ ) is much smaller than the total  $N_0 = N_{\uparrow} + N_{\downarrow}$  number of spins<sup>1</sup>.

### 2.1.1 Absorption of energy

Thermodynamic equilibrium is formed by the interaction of the spins with the environment. What happens if we act on our system with a  $\mathbf{B}_1$  magnetic field as seen above, with the resonant  $\omega_L = |\gamma| B_0 = |g| \mu_0 B_0$  frequency? In this case, as we saw in Section 1.2, transitions occur between the  $|\uparrow\rangle$  and  $|\downarrow\rangle$  states, with probabilities that are equal in both directions ( $W_{\uparrow\downarrow} = W_{\downarrow\uparrow}$ ). Thus the external perturbation distorts the thermodynamic equilibrium: it tries to balance the populations. The interaction of spins and the environment, on the other hand, tries to preserve the Boltzmann distribution. This in turn causes that if the external field has frequency  $\omega = \omega_L$ , energy is continuously drawn from the external field into the medium: the  $B_1$  field does work on the spins when flipping them (since in the equilibrium case  $N_{\downarrow T} > N_{\uparrow T}$ ), and the interaction of the spins with the environment gives off this energy into the environment.

So if the distribution of spins is more balanced than would be in thermodynamical equilibrium (this is the situation when the resonant  $B_1$  field is applied), then there is a continuous energy dissipation from the excitation field. The behavior of a system that is slightly off equilibrium can be described in terms of *relaxation times*: the  $T_1$  spin-lattice relaxation time is the decay constant of the (exponential) regression of the spin system after the cessation of the perturbation that caused the off-equilibrium population.

If the spins are coupled to the environment strongly enough compared to the perturbation, then the spin-lattice relaxation time is much shorter than the time that it would take for the spin populations to become equal as a result of the external perturbation (that causes transitions in unit time with  $W_{\uparrow\downarrow}$  probability):  $T_1 W_{\uparrow\downarrow} \ll 1$ . In this case the spin system will be close to equilibrium even when the perturbing (excitation) field is

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<sup>1</sup> Keeping in mind that the resonance frequencies for electrons are in the domain of microwaves, and those for nuclear spins are in the domain of radio waves, and recalling that at room temperature, the black-body radiation spectrum mainly falls in the infrared region (which is much greater frequency than either microwaves or radio waves), we can immediately arrive at the conclusion, without knowing the actual numbers cited above, that at room temperature, the difference in the occupations is very small compared to the total number of spins.

applied, so according to the above considerations, a continuous energy absorption can be observed. For measuring the resonance this is the desirable condition. If, on the other hand, we increase  $B_1$  and thus  $W_{\uparrow\downarrow}$  to when  $W_{\uparrow\downarrow}T_1 \simeq 1$ , this no longer holds: the distribution will be far from equilibrium (ie. closer to even populations), and the absorption decreases. This phenomenon is called *saturation*. In case of nuclei  $T_1$  can be as high as 1 s, so this can occur readily: this can be remedied by decreasing  $B_1$ , or increasing the coupling of the spins to the environment (to decrease  $T_1$ ); eg. by adding paramagnetic salts to the sample. In case of electron spin resonance saturation occurs rarely because the coupling of the electron spins to the environment is usually much stronger than that of nuclear spins; the  $T_1$  relaxation time here is usually on the order of  $10^{-9}$  s.

So far we demonstrated the energy absorption based on the quantum mechanical treatment seen in Section 1.2. In the classical treatment (Section 1.3.2) this phenomenon can be understood by remarking that the energy stored in the interaction of the spin with the  $\mathbf{B}_0$  homogeneous field will be changed by the  $\mathbf{B}_1$  external field only if  $\omega \approx \omega_L$ . We can thus conclude also in this picture that if  $\omega \approx \omega_L$ , then substantial energy can be given off to the magnetic moment, that eventually drains into the environment. Nonetheless, the quantum mechanical picture gives a more fundamental and realistical description.

### 2.1.2 Frequency dependence of absorption; the shape of the resonance signal

So far we have seen that (according to the quantum mechanical description) we have absorption only in the case when  $\omega = \omega_L$  exactly holds, ie. if we investigate the absorption as a function of the  $\omega$  frequency of the excitation (perturbing) field  $\mathbf{B}_1$ , we get a Dirac delta like dependence. In reality, the measured absorption curve has some width. There are two reasons for this: one is the so-called *homogeneous* broadening, which is related to the finite  $\delta t$  life-time of higher energy states, the other is the *inhomogeneous* broadening, caused by the inhomogeneities in the magnetic field.

Homogeneous line broadening occurs because an excited state with finite  $\delta t$  life-time has, by the Heisenberg uncertainty relation, an energy width  $\delta E \approx \hbar/\delta t$ . The life-time of the excited state (in our case, the  $|\uparrow\rangle$  state, which has higher energy) is strongly connected to the relaxation times, roughly speaking  $\delta t \approx T_1$ . Thus in a given  $B_0$  magnetic field, we see considerable absorption in the frequency domain with  $\delta\omega \approx \delta E/\hbar \approx 1/\delta t$  width around the  $\omega_L$  frequency. The signal shape corresponding to this broadening is typically a Lorentz curve ( $\frac{1}{1+(\omega-\omega_L)^2/(\delta\omega)^2}$ ), known also from the theory of vibrations.

Another cause for the finite line width of the resonance curve is that the spins in the medium feel different magnetic fields. This can stem from the inhomogeneity in the external  $B_0$  field, but what is more important is that even in the case of perfectly homogeneous external field, there is a local magnetic field in the sample that varies from point to point. Its characteristic fluctuation is denoted by  $\delta B_{\text{loc}}$ , this causes a  $\delta\omega = \gamma\delta B_{\text{loc}}$  line width. For example, in the case of dipole-dipole interactions, a magnetic moment  $\mu$  causes a  $\delta H = \mu/r^3$  field at the position of the adjacent spin (in a distance of  $r$ ). For

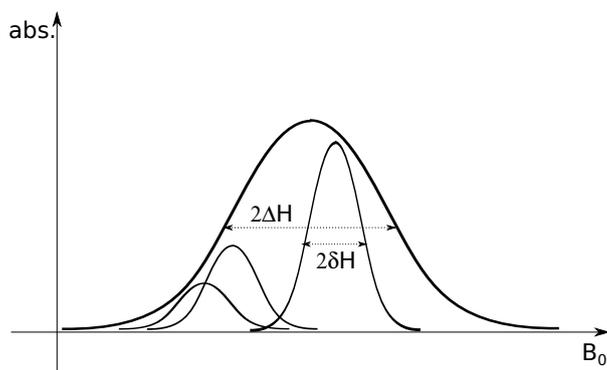


Figure 3: Homogeneous ( $\delta B$ ) and inhomogeneous ( $\Delta B$ ) broadening: the wide, inhomogeneously broadened line shape is the superposition of many shifted lines (with homogeneous broadening).

electrons,  $\mu \approx \mu_B$ , so for  $r = 10^{-10}$  m, we get approx.  $\Delta B = 0.002$  T. Since  $B_0$  is a few tenths of a tesla (or possibly a few teslas), the absorption curve broadens considerably. Sometimes because of this one needs to increase the distance of spins — in case of liquids, by decreasing the concentration of the solution, in case of solids, by implanting the paramagnetic ions into some diamagnetic carrier material.

The line shape characteristic to inhomogeneous broadening is a Gaussian, but because of the homogeneous broadening, we rather have an enveloping curve of many Lorentz curves with  $\delta\omega$  width. It is customary to introduce the  $T_2 = \frac{1}{\gamma\Delta B}$  relaxation time for a given line width. Fig. 2.1.2 illustrates the different line broadenings.

## 2.2 Outlook: application of NMR in chemistry and medicine

Much information can be gained on the structure of a molecule that contains hydrogen by determining the nuclear magnetic resonance spectrum of the proton. Protons in different bonds and molecular groups, and in the vicinity of different atoms feel different local magnetic field, so they resonate at different frequencies. This in turn causes the occurrence of resonance lines at characteristic frequencies. Besides this, protons — through valence electrons — interact with each other. Depending on whether this interaction increases or decreases the local magnetic field (this is determined by the orientation of the spins) the lines split further, generating multiplet lines. Beyond the simple measurement of the spectrum, one can also refine the method by using multiple excitation frequencies, causing one or more lines to saturate (see Section 2.1.1). Thus the split that was caused in other lines by the group just saturated ceases to exist, so one can search for the multiplets belonging together. By the full evaluation of the spectrum, one can even map out the structure of complicated big molecules, usually as part of a complex investigation.

Besides of the proton, there are other nuclei that are useful for the determination of

molecular structure, such as deuterium, fluorine, phosphorus and  $^{13}\text{C}$ . This latter is very much important in the investigation of organic molecules.

With the development of the measurement methods and computational data analysis techniques nuclear magnetic resonance became an indispensable tool in medical diagnostics. During the „measurement“ the patient is in an almost homogeneous magnetic field generated by a solenoid. By changing the inhomogeneity of the field in a very precise manner the resonance condition is satisfied in different slices of the body (the domain where the magnitude of the magnetic field is the desired value, so that the resonant frequency coincides with the excitation frequency, is always a two-dimensional surface). By repeating the measurement multiple times, for different slices, one can explore the three-dimensional absorption map of the body, so just as with an X-ray image, the different organs and their possible deformations become visible. The advantage of this method is that a very accurate picture can be taken without any damage or radiation burden.

### 2.3 Outlook: high resolution pulse mode devices

In the laboratory course we will work with a simple setup that demonstrates nuclear magnetic resonance measurement based on energy absorption. This is a continuous operation device; during operation, when resonance occurs, the sample absorbs energy from the excitation field. The continuous operation has some drawbacks:

- One must change the excitation frequency slowly, with utmost stability, which is technically difficult. It is preferable to use a constant frequency.
- One can use limited excitation power level, because saturation can easily occur.
- There is no simple method to increase the signal to background ratio.

Because the last two reasons, dilute and/or not easily excitable nuclei are almost impossible to measure, because the signal simply does not emerge out of the noise.

Modern devices operate in pulse mode: this overcomes all three problems mentioned above. In industrial, medical and high level research applications, pulse mode devices have almost completely replaced the continuous operation devices.

In a pulse mode measurement first one gives a high power (few kW), short (a few tens of  $\mu\text{s}$ ) pulse to the sample, close to the Larmor frequency. From the theory of vibrations it is known that the frequency spectrum of such a pulse is wide (its width is roughly the inverse of the time duration of the pulse), so we can view the situation as that we excite all the different resonant frequencies of the sample close to each other, in the whole frequency domain to be investigated. After the pulse, during detection, we measure the time dependence of the magnetization induced in the sample; this of course decays with a decay constant  $T_1$ . The time dependence of the magnetization is the Fourier transform of the resonance spectrum (since we had excited the whole frequency

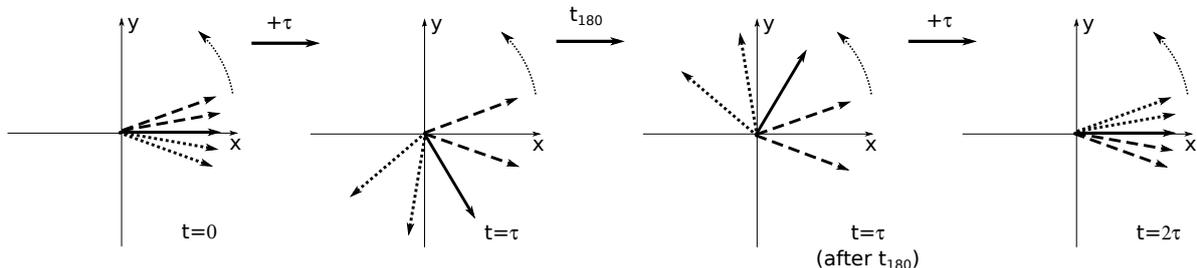


Figure 4: Illustration of the time evolution of magnetic moments in spin echo experiments.

domain in a coherent manner), so taking the Fourier transform of the magnetization we can deduce the resonance spectrum. The total time required for the measurement is at most a few seconds: adding many measured signals one can greatly enhance the signal to background ratio.

## 2.4 Outlook: spin echo experiments

For the sake of completeness we briefly review the spin echo technique mentioned in Section 2. To understand this, we make use of the classical treatment of the motion of spins (Section 1.3), which is valid also for the expectation values of the corresponding quantum mechanical operators as well.

Spin echo experiments also operate in pulse mode: at the beginning the sample is in a static, homogeneous  $\mathbf{B}_0$  field (pointing in the  $z$  direction). During the measurement, we give an excitation field that points in the  $x$  direction, has  $B_1$  amplitude,  $\omega_L = \gamma B_0$  Larmor frequency, and lasts for a given  $t$  time. As before,  $B_1 \ll B_0$ , and  $t \gg 1/\omega_L$ . If first we give a pulse to the sample that lasts for

$$t_{90^\circ} \equiv \frac{\pi/2}{\gamma B_1},$$

which is called a „90° pulse. This rotates the magnetization (all spins) into the  $x$ - $y$  plane (as illustrated on Fig. 2.4), and they begin to precess with  $\omega_L$  frequency. We can detect this using a coil standing in the  $y$  direction (the precession induces voltage in this). Fig. 2.4 shows a typical spin echo experimental setup. The Larmor frequencies of the individual spins are a bit different from each other, as discussed in Section 2.1.2 (characteristically  $\Delta\omega = \gamma\Delta B_{\text{loc}}$ , because of local fluctuations in the magnetic field). This causes some of the spins to advance, and some to fall behind: it is easy to see that the resultant magnetization decreases in time with decay constant  $T_2$  introduced in Section 2.1.2, thus the voltage induced in the coil in the  $y$  direction also decreases.

After an arbitrary  $\tau$  time elapsed (that is on the order of  $T_2$ ), one gives a so called

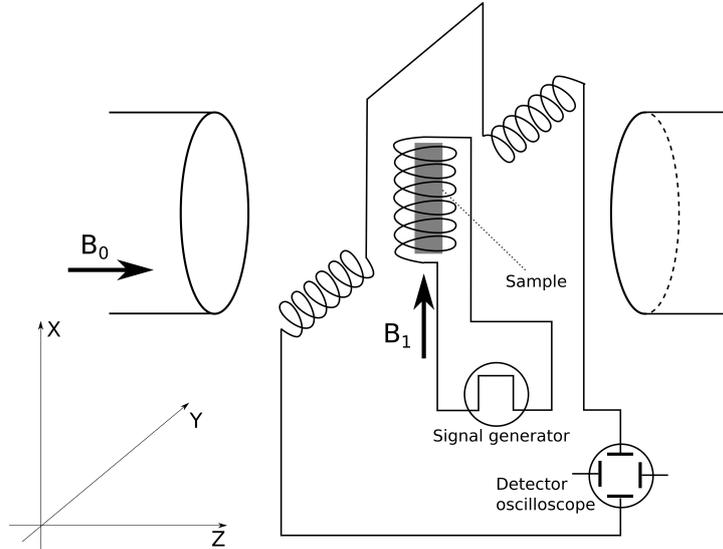


Figure 5: Conceptual diagram of a spin echo experiment.

$180^\circ$  pulse to the sample, ie. a pulse that lasts for

$$t_{180^\circ} \equiv \frac{\pi}{\gamma B_1}.$$

Technically  $t_{180^\circ}$  is much less than  $\tau$ . During this pulse, the spins rotate by  $180^\circ$  around the  $x$  axis (we assumed that the  $\mathbf{B}_1$  field points in the  $x$  direction). So the spins rotating in the  $x$ - $y$  plane switch places: those that fell behind get to the front, and those that advanced, get to the back.

So the spins that diverged up to now, begin to converge (since the fluctuations in the local magnetic field remain the same). After a  $\tau$  time passing again, we again get an ensemble of coherently precessing spins: the process leading to divergence now proceeds back in time. In the detecting coil we again get bigger induced voltage. Fig. 3.1 shows the time development of the excitation pulses and the measured signals. The name „spin echo” is now understood: the excitation at  $t = 0$  „reflects” on the one  $\tau$  time later, and generates a signal after  $2\tau$  time (an „echo”). The process can be repeated: with another  $180^\circ$  pulse at  $3\tau$  and  $5\tau$ , we get echoes at  $4\tau$  and  $6\tau$ . The amplitude of these latter echoes will be smaller due to the relaxation processes ( $T_1$ ), so in this experimental method one is able to directly measure the  $T_1$  relaxation time.

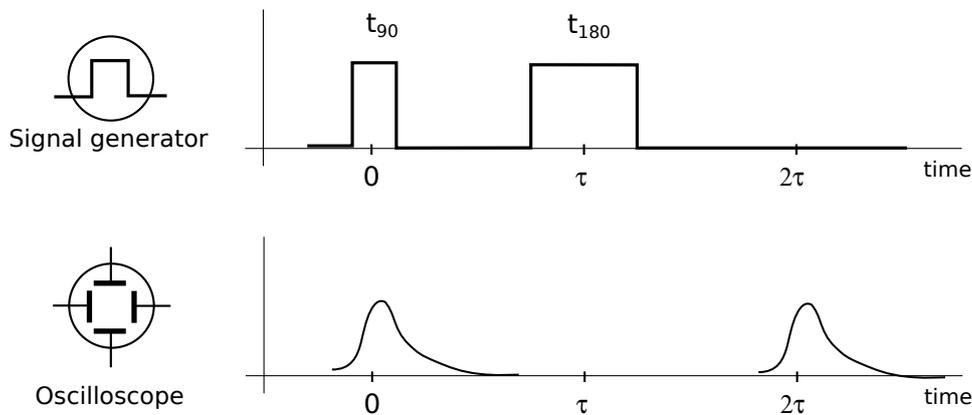


Figure 6: Spin echo experiments: pulses given off to the sample and „reflected” signals.

### 3 Measurement of nuclear magnetic resonance in the laboratory

The goal of the laboratory course is to demonstrate the phenomenon of nuclear magnetic resonance and to investigate the basic concepts of it. The apparatus follows the philosophy of „demonstration: contrary to the commercially available, high resolution devices our setup consists of simple components that are thus easy to study and make the operation of the setup easily understandable.

#### 3.1 Short description of the measurement apparatus

Resonance needs a homogeneous magnetic field, which is produced here by a big iron core electromagnetic coil with many thousand turns, with some 0.5-2 A DC flowing through it. To make the resonance better visible, the DC (and the magnetic field) is modulated with a 25 Hz harmonic signal with an amplitude of 1-2 % of the original field. (For this purpose, a separate coil is built in the magnet.)

We use the same coil for detecting the absorption due to resonance that is used for the radio frequency excitation. This coil is in an oscillator circuit, the decrease of the amplitude of this oscillator signifies the absorption. The resonance is displayed on an oscilloscope: to deflect the electron beam, on the horizontal axis we use the modulation of the homogeneous magnetic field, on the vertical axis we use the absorption measured by the oscillator. When the homogeneous magnetic field reaches the resonance condition (this is determined by the constant frequency of the oscillator), the absorption peak appears on the oscilloscope. We use two samples: for proton resonance, we use water (mixed with a paramagnetic salt — cupric sulfate), and a teflon sample for the resonance of fluorine.

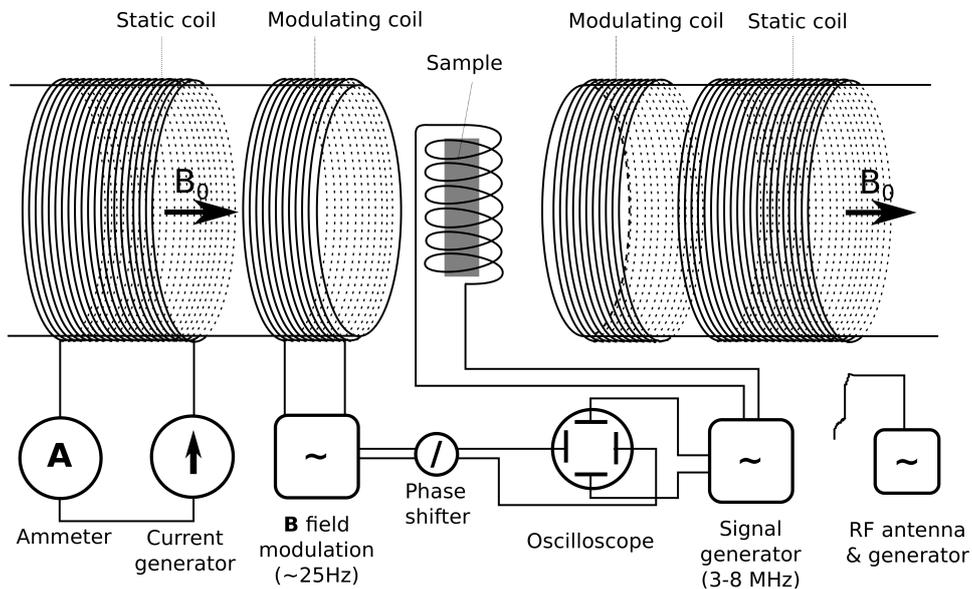


Figure 7: Schematic diagram of the measurement apparatus used in the laboratory course. The homogeneous current and the field modulating current flow through the coils on both sides, for the sake of clarity we omitted here the symbols of the wires from the coils on the right hand side.

It is important to note that because of the high inductance of the coil that produces the modulating field, the voltage on it will be out of phase with the current flowing on it. So for the horizontal axis of the oscilloscope to display the actual value of the modulating field (ie. the current flowing through the modulating coil), we need to manually shift the phase of the modulating voltage before when given onto the oscilloscope.

### 3.2 Turning on the apparatus

The first few steps of the measurement are

- Turn on the radio frequency oscillator — by plugging its adapter to the power outlet. After a few seconds the (single) needle on the front of the device should show the pre-set value. In what follows, the only thing to change with this device is the excitation frequency, using the disk at the side of the box.
- Next step is turning on the electromagnet. Before it make sure that the current regulator (the turning knob at the front of the power supply) is set to the lowest current. Turn on the multimeter used for current measurement (it should of course show nearly zero), and then turn on the power supply of the electromagnet using

the switch at the back of the box. Check that turning the current regulator knob causes current to flow through the coil, and it is shown by the current meter!

- Turn on the generator that modulates the homogeneous magnetic field, using the button at the back of the box. After turning it on, press the „Reset” button, after which the oscillation stabilizes: the frequency should be 25 Hz (on the left display), voltage should be some 12-15 V (right display).
- Turn on the oscilloscope with the red on-off button! If everything is OK, after warming up it will show a horizontal, slightly noisy signal line.
- Put the water sample (slightly blueish glass vial) into the small coil of the oscillator! This coil should be placed exactly into the center between the faces of the electromagnet, the sample inside the excitation coil, fully plugged in.
- Search for the resonance! Set the oscillator frequency (using the frequency button) to approximately 6 MHz (the scale on the button makes it possible to read off the value). Increase the current in the electromagnet slowly to approx. 1.5 A! Around 1.3 A we should see the absorption peak wander through the oscilloscope screen.
- Turn on the signal generator that will be used to determine the frequency of the oscillator, using the button at the back of the device!
- Connect the ballistic galvanometer to the line power. This will be used for the measurement of the magnetic field. It has a mirrored display, we should see it as a light stripe on the scale of the instrument. (The dark line in the center of the light stripe shows the measured value.)

In this measurement we want to verify some basic expectations (so to say, simple theoretical predictions) about magnetic resonance. Resonance is connected to the excitation frequency and the magnetic field, so we must measure these quantities.

The measurement of the oscillator frequency is done by comparing it to a known frequency produced by the signal generator. For this, we borrow the fruitful concept of „beat” from radio technology: when adding two signals with almost the same but slightly different frequency, it produces a measurable low-frequency beat. The signal from the signal generator couples to the signal of the oscillator through an antenna, a short free wire. The frequency of the signal generator can be read off from its display, in units of MHz. Its value can be changed with the „up” and „down” buttons in coarse steps, and can be fine tuned with the „fine” button. At the beginning of the frequency measurement set the amplitude to the maximum! One should then change the frequency in coarse steps, and look for the instant when on the oscilloscope one sees the beat (like a flash). With the fine tuning we can search the beat more accurately — for this, because

of the higher intensity, we should lower the amplitude of the signal generator. (This process needs some experience — if problematic, the laboratory instructor can help.)

We measure the magnetic field with a ballistic galvanometer, by measuring the induced voltage in a small coil. This works as follows. According to the Maxwell equations, the time integral of the voltage induced in a coil is equal to the change in the magnetic flux through the coil. If the coil has ohmic resistance, then proportionality holds also for the time integral of the current in the coil. The galvanometer is a device that measures the charge that passed through, and shows the result by the swing of the light stripe. The measurement is done by inserting the galvanometer coil between the faces of the electromagnet, and when the jitter of the light stripe ceases, we pull it out. From the maximal displacement of the dark line at the center of the light stripe we can determine the value of the magnetic field. The calibration constant here is 3.025 mT/division.

### 3.3 Measurement tasks

**1. Measurement of the resonance of the proton.** Measure the resonance frequency of the proton sample and the corresponding magnetic field in 12-14 different points evenly scattered in the whole frequency domain attainable for the oscillator (3.5 MHz – 8 MHz). Verify the linear relationship. Determine the  $g$  factor of the proton.

**2. Comparative measurement of the resonance of fluorine.** For 3-4 different points determining the ratio of the  $g$  factors of the proton and that of fluorine. We do this by holding the magnetic field at a constant value, while measuring the resonant frequencies of the proton and of fluorine, so the uncertainty of the magnetic field cancels in the ratio. The  $g$  factor of fluorine is 5-10% less than that of the proton, this may help in finding the weaker resonance of the fluorine.

**3. Estimation of the systematic uncertainties.** Do a detailed investigation of the systematic errors and uncertainties in the measurement. Estimate the values of them, and give an explanation on this. Explore the main sources of uncertainties. If some source of error is negligible, it is enough to give a brief explanation. It is important though that the potentially significant errors (measurement of the magnetic field, of the frequency, the frequency stability of the oscillator, read-off errors, etc) are to be accurately estimated, (perhaps using more than one method), and their effect on the results (such as the  $g$  factors) must be carefully analyzed. This topic is a task in itself because the measurement setup is very transparent and simple, so all the different sources of uncertainties can be found simultaneously with the measurement.

**4. Estimating the inhomogeneity of the magnetic field.** The resonance can best be observed if the magnetic field is homogeneous: inhomogeneities make the peak wider and decrease its amplitude (so decrease signal to background ratio). Let's measure the inhomogeneity of the magnetic field used in our experiment (or give an upper limit to it), for example, what's the deviation of the magnetic field at the edge of the sample, or

in a distance of 1 cm from the center of the magnet. (The „definition” of inhomogeneity can be altered rather arbitrarily, but it is important that it must be reproducible.) Use two different methods: a direct estimation by moving the sample away from the center, and an indirect one, from the visible width of the peak. Describe in detail how do we compare to the signal seen on the oscilloscope, for example, how we determine the frequency difference corresponding to one axis unit on the screen of the oscilloscope.

### 3.4 Some common problems and solutions, some caveats

There are some problems that frequently come around during the measurement. We detail some of them, and also some potentially dangerous actions that are to be avoided.

- Be aware that one should **never, ever break** the circuit of the electromagnet, even out of negligence! The electromagnet has a very high inductance, breaking the circuit generates a voltage spike that can cause electric shock or destroy the power supply.
- Sometimes the sample slides out of the excitation coil of the oscillator. We should check for this every once in a while.
- When measuring the frequency, the amplitude of the signal generator should be turned on! It can be very annoying if we do not find the beat because the signal generator does not give off any signal. When searching for the resonance, the amplitude should be back down, in order not to cause unnecessary noise!
- At smaller frequencies, below 4.5 MHz, the signal starts to diminish, the cause of this is the drop in the efficiency of the excitation coil. In this domain we can only see the resonance of the proton. The peak can be found in the whole domain, down to the smallest frequencies (3.5 MHz), here we must do the measurement with the necessary care. The measurement of the frequency also gets cumbersome in this domain (the efficiency drop of the antenna is to be blamed). As a matter of fact, the measurement can be done in this domain, don't give up. It is of some help if someone grabs the output wire of the signal generator, him- or herself acting as an antenna.
- The excitation coil that envelops the sample should always be positioned exactly in the center (in particular, centered in the direction of the homogeneous magnetic field) between the faces of the magnet. This is important for the reproducibility of the measurement; the capacitive coupling between the magnetic core metal and the coil causes a frequency shift, and thus a shift of the peak (this problem also shows up in the measurement of the field homogeneity).

- If the frequency of the modulating magnetic field and/or the phase shift in the signal given to the horizontal axis of the oscilloscope is not set correctly, the voltage measured on the oscilloscope will be out of phase with the modulating magnetic field (see Section 3.1). This will cause that instead of one, there will be two different „resonance peaks” visible on the oscilloscope screen. Be aware of this!

### 3.5 Control questions

1. What is the phenomenon of nuclear magnetic resonance?
2. What method do we use to measure the frequency of nuclear magnetic resonance?
3. What is the principle and the method of the measurement of the magnetic field?
4. What is the relation between the resonance frequency of the proton (or a nucleus) and the magnetic field?
5. What are the conditions, the methods, the difficulties, and the possible dangers of producing a homogeneous magnetic field?
6. What conditions are to be met in order for us to be able to observe the resonance?
7. What is the  $g$  factor? How can we determine it?
8. What is the order-of-magnitude relation between the resonance frequency of an electron and that of a nucleus in a given magnetic field?
9. What are the domains of the magnetic field and of the frequency where resonance can be observed?
10. How can we estimate the magnitude of the different errors and uncertainties (read-off, measurement, statistical...)? What are the important sources of uncertainty in the determination of the  $g$  factor?
11. What are the main sources of error in the determination of the ratio of  $g$  factors?
12. Which are those cable connections in the measurement setup that are not to be disconnected at any time?

## References

- [1] J. Keeler (2005). Understanding NMR Spectroscopy. John Wiley & Sons. ISBN 0-470-01786-4.