Lecture 13.
Spin-resonance and spin-relaxation

The purpose of this lecture is to give an introduction to the immensely rich field of magnetic resonance and spin-relaxation. Due to its volume and importance, this subject forms a field of its own. It seem correct that any qualified physicist should know its basic ideas.

Spin Resonance

Consider a system of spins weakly interacting with each other and with the thermal bath. In external uniform magnetic field $\mathbf{B}$ the total spin $\mathbf{S}$ evolves as

$$\frac{\partial \mathbf{S}}{\partial t} = \gamma[\mathbf{B} \times \mathbf{S}] + \frac{i}{\hbar}\,[\mathcal{H}_{\text{int}}, \mathbf{S}], \tag{1}$$

where the first term describes the Larmor precession of spins in magnetic field (γ is the gyromagnetic ratio), while the second term describes interactions with the environment, which lead to different sorts of relaxation, splittings and all that.

A typical setup for the spin resonance consists of a steady field $\mathbf{B}_0$ (we choose the z-axis along this field) and a perpendicular to it circularly polarized field $\mathbf{B}_\perp$ ($\mathbf{B}_\perp \cdot \mathbf{B}_0 = 0$) which varies harmonically with time:

$$B_\perp^\pm = B_x \pm iB_y = be^{\pm i\omega t}.$$

Felix Bloch was the first to introduce phenomenologically different relaxation times for longitudinal S_z and transverse $S_\pm = S_x \pm iS_y$ components of spin $\mathbf{S}$. In these components Eq (1) takes the form:

$$\frac{\partial S_z}{\partial t} = -\frac{S_z - \bar{S}}{\tau_1} + i\gamma \left(B_+ S_- - B_- S_+ \right), \quad \bar{S} = \chi B_0; \tag{2}$$

$$\frac{\partial S_\pm}{\partial t} = \pm i\Omega \ S_\pm - \frac{S_\pm}{\tau_2} \mp i\gamma S_z B_\perp^\pm, \quad \Omega = \gamma B_0. \tag{3}$$

Here χ is the static spin susceptibility. The spin components S_i obey the normalization condition

$$S_z^2 + S_+ S_- = 1. \tag{4}$$

Under time dependent pumping, the system of spins adsorbs energy Q per unit time. Since the energy $E = -\gamma \mathbf{BS}$, the rate of dissipation Q is

$$Q = -\frac{dE}{dt} = \gamma B_0 \langle \, \frac{\partial S_z}{\partial t} \rangle + \gamma b \langle \, \frac{\partial S_-}{\partial t} e^{i\omega t} + \frac{\partial S_+}{\partial t} e^{-i\omega t} \rangle =$$
$$= \gamma B_0 \frac{\bar{S} - \langle S_z \rangle}{\tau_1}, \tag{5}$$

where the brackets $\langle..\rangle$ denote averaging over the period of external pumping. We can see that pumping leads to a difference between the equilibrium polarization $\bar{S}$ and dynamic polarization $\langle S_z \rangle$ which relaxes with the relaxation rate τ_1. This causes dissipation.
In the linear approximation in b

$$S_{\pm} = \frac{i\gamma b S_z}{\Delta\omega \pm i/\tau_2}\, e^{\pm i\omega t}, \quad S_z = \chi B_0, \quad \Delta\omega = \Omega - \omega. \quad (6)$$

Therefore, the transverse relaxation rate gives the width of the resonance in the linear response regime.

Saturation. Longitudinal and transverse relaxation rates

Under any conditions, we will assume in this lecture that both relaxation rates are relatively small ($\Omega\tau_{1,2} \gg 1$). This allows to assume that the a.c. field b is much weaker that the steady field B_0 ($b \ll B_0$) in both linear and non-linear regimes. Under these conditions, $\dot{S}_z = 0$ and $S_{\pm} \propto e^{\pm i\omega t}$, which leads to the equation

$$\frac{S_z - \bar{S}_z}{\tau_1} = \frac{i\gamma b}{2}\left(S_+ e^{-i\omega t} - S_- e^{i\omega t}\right), \quad (7)$$

which gives, together with Eqs (2, 3):

$$S_{\pm} = \frac{i\gamma b S_z}{\Delta\omega \pm i/\tau_2}\, e^{\pm i\omega t}; \quad (8)$$

$$S_z = \chi B_0\, \frac{1 + \tau_2^2 \Delta\omega^2}{1 + \tau_2^2\Delta\omega^2 + \gamma^2 b^2 \tau_1\tau_2} \quad (9)$$

As a result, the dynamic susceptibility $\chi(\omega) = \chi'(\omega) + i\chi''(\omega)$ takes the form

$$\chi'(\omega) = \chi\frac{\Omega\tau_2}{2}\frac{(\Omega-\omega)\tau_2}{1+\tau_2^2(\Omega-\omega)^2+\gamma^2 b^2\tau_1\tau_2}; \tag{10}$$

$$\chi''(\omega) = \chi\frac{\Omega\tau_2}{2}\frac{1}{1+\tau_2^2(\Omega-\omega)^2+\gamma^2 b^2\tau_1\tau_2}. \tag{11}$$

The rate of dissipation is equal to

$$Q = \chi\ b^2\ \frac{\Omega^2\tau_2}{1+\tau_2^2(\Omega-\omega)^2+\gamma^2 b^2\tau_1\tau_2}. \tag{12}$$

We can see from Eqs (10), (11) and (12) that $1/\tau_2$ gives the width of the absorption line in the linear regime when dissipation is proportional to the intensity of pumping b^2. When pumping exceeds the scale

$$(b^2)_{\mathrm{sat}} \sim \frac{1}{\gamma^2\tau_1\tau_2}, \tag{13}$$

the dissipation saturates, because the occupation numbers for spin up and spin down are nearly equal. The spectral position of the resonance does not change, while the width of the resonance line grows to

$$\langle\Delta\omega\rangle^2 = \frac{1+\gamma^2 b^2\tau_1\tau_2}{\tau_2^2} \rightarrow_{b\rightarrow\infty}= \frac{\gamma^2 b^2\tau_1}{\tau_2}. \tag{14}$$

As it has been explained, τ_1^{-1} is the rate of the processes leading to the relaxation of the z-component of spin to its equilibrium value. Due to the constraint (4), all these processes also lead to the relaxation of the transverse components of spin. Therefore, $\tau_2 \leq \tau_1$. Specific processes (see the problems) can occur, leading to dephasing of the coherent precession of the transverse components and leaving the longitudinal components untouched. If the mentioned processes are fast, then $\tau_2 \ll \tau_1$. Under these conditions, nonlinearity (saturation) occurs at weaker pumping b^2, than one could expect from the line-width in the linear response regime. Under the condition of saturation, the pumping induced rate of transition between the spin up and spin down states is larger than the relaxation rate. This means that the effective spin temperature

$$T_s = T(1 + \gamma^2 b^2 \tau_1 \tau_2) \tag{15}$$

may be introduced in order to describe the occupation of quantum states under pumping.

Spin echo

If the difference between the relaxation times $\tau_2 \ll \tau_1$ is large, it is possible to observe an interesting nonlinear phenomenon, called "spin echo".

Let us assume that the system is in the state of equilibrium in the presence of a strong steady field $\mathbf{B}$. Let it experience the effect of a of short pulse of the a.c. field $\mathbf{B}_\perp (\mathbf{B}_\perp \mathbf{B} = 0)$ of duration δt being shorter than all the relaxation times. Initially, the spin is polarized along the z axis. If the duration of the pulse is chosen so that $\gamma B_\perp \delta t = \pi/2$ (90^o-signal), then at time $t > \delta t$, when the a.c. field is switched off, the parallel spin polarization is zero and the spin $\mathbf{S}$ precesses in

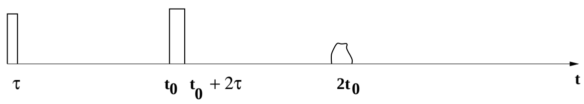

Figure 1: Scheme of experiment on spin echo

the perpendicular plane. So, a signal of induction could be observed at $t > \delta t$ until it dies out at $t \gg \tau_2$. Nevertheless, the absence of this signal does not mean that the occupation numbers of the states with different z-projections of spin are back at equilibrium. Quite the opposite, if $\tau_2 < t < \tau_1$, they have not yet relaxed at all. Zero signal of induction simply means that all individual spins precess in the perpendicular plane, but they are out of phase. If after the expectation time t_0 a 180^o-signal of the resonant a.c. field and of the duration $2\delta t$ is applied, then all these spins change their polarization to the opposite and continue to precess. In the time t_0 after the second signal, the precessing spins get again in phase and it shows itself in the appearance of a new signal of induction (echo) (see Fig 1). This type of experiment with different expectation times t_0 can be used for the measurements of the relaxation time τ_1.

Resonance in the system of electron and nuclear spins.

We are moving on to a set of problems, caused by resonances in the system of nuclear and electron spins coupled by hyperfine interaction. For an atom or an ion with the spin $\mathbf{S}$ [1] and a nuclear momentum $\mathbf{I}$ the Hamiltonian of the hyperfine interaction is

$$\mathcal{H}_h = A\;\mathbf{I}\;\mathbf{S}, \tag{16}$$

which, in the presence of external magnetic field H has to be unified with the Zeemann Hamiltonian

$$\mathcal{H}_Z = -\mu_n \mathbf{I}\;\mathbf{H} - \mu_e g \mathbf{S}\;\mathbf{H}. \tag{17}$$

If $H = 0$, the energy levels are characterized by the total spin $\mathbf{F} = \mathbf{S} + \mathbf{I}$ of the whole system.

$$E_F(0) = \frac{A}{2}[F(F{+}1){-}S(S{+}1){-}I(I{+}1)], \quad |I{-}S| \le F \le S{+}I.$$

A weak magnetic field leads to the splitting of these F-multiplets:

$$E_F(H) = E_F(0) - \mu_e g_h H F_z,$$
$$g_h = g\frac{F(F+1) - S(S+1) + I(I+1)}{2F(F+1)},$$

where the small ratio of the nuclear and electron magnetons, $\mu_n/\mu_e \sim 10^{-3}$, is taken into account.

In the case of a strong magnetic field, $\mu_e H \gg A$, the hyperfine interaction may be neglected and the energies are

$$E_Z = -H[\mu_n I_z{+}\mu_e g S_z]{+}A S_z I_z; \quad -S < S_z < S; \quad -I < I_z < I.$$

[1] In solid, atoms or ions experience the action of the crystalline field. This field affects mostly the orbital motion of electrons which leads to splitting of all degenerate levels. If the splitting is large, all resonance phenomena occur within the lowest level of the splited orbital multiplet. This is described as a frozen orbital momentum. If the lowest level corresponds to a singlet, then the total angular momentum $\mathbf{J} = \mathbf{S} + \mathbf{L}$ is, indeed, reduced to spin $\mathbf{S}$ only. It might happen that the lowest level corresponds to a triplet or quartet. In this case, it is customary to speak about "effective" spin, which differs from the real one by having the gyro-magnetic factor g equal neither to one nor to two.

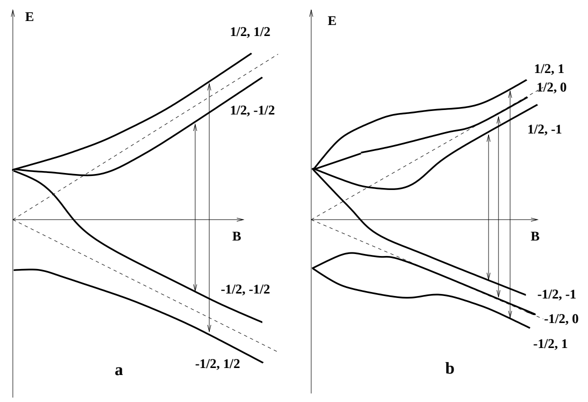

Figure 2: Terms of electron/nuclear spin sistems for I = 1/2, S = 1/2 (a) and for I = 1, S = 1/2 (b).

Examples of the terms of the electron-nuclear spin system for $I = 1/2$ and $S = 1/2$ and for $I = 1$ and $S = 1/2$ are shown in Fig 2. We have neglected the Zeemann energy of nuclear spins, because of the small ratio $\mu_n/\mu_e \sim 10^{-3}$. So, all lines in Fig 2, corresponding to the same values of S_z, are parallel. The hyperfine splitting of the electron spin levels leads to the hyperfine splitting of the line of the electron spin resonance. It is important, though, to remember that those transitions, for which $\Delta S_z = \pm 1, \Delta I_z = 0$, have the largest oscillator strength and are major permitted transitions. These lines correspond to the splitting of the ESR line into equidistant lines of frequencies

$$\hbar\omega = g\mu_e B + AI_z$$

The transitions with $\Delta S_z = \pm 1, \Delta I_z = \pm 1$ have the strength in $(A/g\mu_e B)^2$ times smaller than the major transitions. These transitions can be induced, if the a.c. field and the

constant field are parallel and the major transitions are absent. Purely nuclear spin transitions with $\Delta S_z = 0, \Delta I_z = \pm 1$ are also suppressed by the factor $(A/g\mu_e B)^2$ compared to the major transitions, but they belong to a very different frequency range and therefore are easily separable from conventional ESR transitions.
Using nonlinearity of the system of electron and nuclear spins, one can st up several interesting experiments.

Dynamic Orientation of Nuclei

There are two parameters, coupled to nuclear spins: nuclear spin polarization

$$P_1 = \frac{\langle I_z \rangle}{I}$$

and nuclear spin aligning

$$P_2 = \frac{\langle 3I_z^2 - I(I+1) \rangle}{3I^2 - I(I+1)} = \frac{\langle 3I_z^2 - I(I+1) \rangle}{I(2I-1)}.$$

The latter characterizes the preference for spin to be oriented either along the z-axis or in the perpendicular plane, irrespective of their directions.
It is very difficult to achieve either nuclear spin polarization or aligning using external magnetic field, because of a very weak coupling of nuclear spins to electric and magnetic fields, available in laboratories. We will consider two methods in which the spin resonance ideas are used.
Consider, as an example, a system with $I = 1, S = 1/2$. Let the temperature and magnetic field obey the condition

$T \gg \mu_e g B \gg A$ ($\delta_e = g\mu_e B/T \ll 1$). Then there is no nuclear spin polarization (aligning) at equilibrium. Electron spin polarization is not zero but small (of the order of δ_e). The key role is played by the spin-lattice relaxation of the nuclear spins. The rate of this relaxation is of the order of $1/\tau_1$ for the transitions with $\Delta S_z = \pm 1, \Delta I_z = 0$ and of the order of $(A/g\mu_e B)^2/\tau_1$ for so called "flip-flop" transitions with $\Delta(I_z + S_z) = 0,\ \ \Delta S_z = \pm 1, \Delta I_z = \mp 1$. All other channels of relaxation are practically forbidden. The detailed balance of the electron and nuclear spin relaxation through the permitted and the "flip-flop" processes leads to the following conditions for the occupation numbers $N(S_z, I_z)$:

$$\frac{N(+1/2, I_z)}{N(-1/2, I_z)} = \exp\left[-\frac{g\mu_e B}{T}\right] = 1 - \delta_e, \tag{18}$$

$$\frac{N(+1/2, I_z - 1)}{N(-1/2, I_z)} = \exp\left[-\frac{g\mu_e B}{T}\right] = 1 - \delta_e. \tag{19}$$

Therefore, at the equilibrium, the occupations of all electron-nuclear levels are $1 \pm \delta_e/2$ for $S_z = \pm 1/2$ and irrespective of I_z. If the perpendicular a.c.pumping is done at the resonant frequency and the condition of saturation for, say, $I_z = 1$ is fulfilled, then we have equal occupations of the states $S_z = \pm 1/2, I_z = 1$. Due to nuclear spin lattice relaxation, this leads to the redistribution of the population at the other electron-nuclear levels. Using Eqs (18) and (19), we arrive at the following table of the occupation numbers under the condition of saturation:

$$N(\pm 1/2, 1) = N(-1/2, 0) = N(-1/2, -1) = 1 + \frac{\delta_e}{3},$$

$$N(1/2,0) = N(1/2,-1) = 1 - \frac{2\delta_e}{3},$$

Then the polarization P_1 and aligning P_2 are:

$$P_1 = \frac{\delta_e}{6}, \qquad P_2 = \frac{\delta_e}{6}.$$

A similar method of dynamic polarization of nuclei consists in the pumping at resonant frequency of one of the “flip-flop” transition and saturation of this resonance. This method allows to use a faster channel of relaxation then in the method considered above.

Double Electron-Nuclear Spin Resonance

Consider an electron-nuclear system in the presence of two a.c.fields $\mathbf{B}_1$ and $\mathbf{B}_2$. The frequency of one of the fields is close to that of the electron spin resonance and that of the nuclear spin resonance for a given static field $\mathbf{B}$. Since the times of spin-lattice relaxation are fairly large, changing the magnetic field $\mathbf{B}$, one can accomplish saturation of both transitions. In the system $S = 1/2,\ I = 1$, familiar to us, the saturation leads to the following table of the occupation numbers:

$$N(\pm 1/2,1) = N(1/2,0) = N(1/2,-1) = 1 - \frac{\delta_e}{3},$$

$$N(-1/2,0) = N(-1/2,-1) = 1 + \frac{2\delta_e}{3}.$$

A remarkable feature of this table is that

$$N(-1/2,1) - N(-1/2,0) = -\delta_e.$$

As a result, the oscillator strength of this transition becomes approximately δ_e/δ_n times larger. Usually, even this enhancement is not sufficient for direct observation of the transition between two states with different polarizations of nuclear spin. Nevertheless, the scheme can be inverted: accomplishing the saturation of the nuclear spin transition, we change the intensity of the much stronger electron spin resonance.