

Continuous Wave Magnetic Resonance

In this lecture we transform the Bloch equations to the rotating frame to simplify the description of the spin system in the presence of electromagnetic radiation. We then discuss how the magnetization vector moves during resonant and slightly off-resonant irradiation. Up to this point, the physics is the same for NMR and EPR experiments. After this we consider the effect of continuous irradiation of the spin system over times that are much longer than the transverse and longitudinal relaxation time. This part is relevant mainly for EPR spectroscopy, where such *continuous-wave* (CW) measurements are the standard experiment. We discuss shortly, how a CW EPR spectrometer works and why the derivative of the absorption spectrum rather than the absorption spectrum itself is detected.

1 Motion of the Magnetization Vector during Irradiation

1.1 Bloch Equations in the Rotating Frame

At thermal equilibrium, the magnetization vector is parallel to the magnetic field, i.e., it is directed along z . The components M_x and M_y are zero. According to equations (1.24)-(1.26), only the field components B_x and B_y can perturb this equilibrium. In other words, transitions between the two spin states are induced by a *transverse* field in the xy plane. Experimentally it is most simple to generate a linearly polarized field. If we chose the direction of this field along x , the sum of the static longitudinal and the oscillatory transverse magnetic fields is given by

$$B_x(t) = 2B_1 \cos(\omega_{\text{osc}}t) , \quad (2.1)$$

$$B_y(t) = 0 , \quad (2.2)$$

$$B_z(t) = B_0 . \quad (2.3)$$

Solving the Bloch equations with such a time-dependent field is difficult. Therefore, we try to obtain a time-independent field by a coordinate transformation. First, we write the linearly polarized field as a sum of right-handed and left-handed circularly polarized fields,

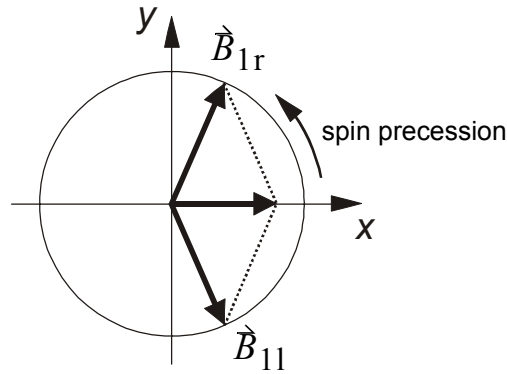
$$\vec{B}_1(t) = 2B_1 \cos(\omega_{\text{osc}}t) \vec{e}_x = \vec{B}_{1r}(t) + \vec{B}_{1l}(t) , \quad (2.4)$$

where

$$\vec{B}_{1r}(t) = \cos(\omega_{\text{osc}}t)\vec{e}_x + \sin(\omega_{\text{osc}}t)\vec{e}_y , \quad (2.5)$$

$$\vec{B}_{1l}(t) = \cos(\omega_{\text{osc}}t)\vec{e}_x - \sin(\omega_{\text{osc}}t)\vec{e}_y . \quad (2.6)$$

One of these components rotates with the same sense as the magnetization vector precesses. Only this component is effective in inducing transitions. The other, counterrotating component can be neglected in a good approximation. Without loosing generality we keep $\vec{B}_{1r}(t)$ and neglect $\vec{B}_{1l}(t)$.



The time-dependent magnetic field $\vec{B}_0 + \vec{B}_{1r}$ is now given by the components

$$B_x(t) = B_1 \cos(\omega_{\text{osc}}t) , \quad (2.7)$$

$$B_y(t) = B_1 \sin(\omega_{\text{osc}}t) , \quad (2.8)$$

$$B_z(t) = B_0 . \quad (2.9)$$

Now we consider the situation in a coordinate frame that rotates counterclockwise with angular frequency ω_{osc} about the z axis of the original laboratory frame. In this *rotating frame*, $\vec{B}_{1r}$ is time-independent,

$$B_x = B_1 ,$$

$$B_y = 0 .$$

As the rotating frame is not an inertial frame, we must be careful about converting B_z . The motion of the magnetization vector induced by the static field B_0 in the laboratory frame (equations (1.20)-(1.23)) is a precession with frequency ω_0 . As the rotating frame rotates with the same sense, the magnetization vector precesses in this frame only with the *resonance offset*

$$\Omega_0 = \omega_0 - \omega_{\text{osc}} . \quad (2.10)$$

Thus, the rotating frame Bloch equations are

$$\frac{dM_x}{dt} = -\Omega_0 M_y - \frac{M_x}{T_2} , \quad (2.11)$$

$$\frac{dM_y}{dt} = \Omega_0 M_x - \omega_1 M_z - \frac{M_y}{T_2} , \quad (2.12)$$

$$\frac{dM_z}{dt} = \omega_1 M_y - \frac{M_z - M_0}{T_1} , \quad (2.13)$$

where

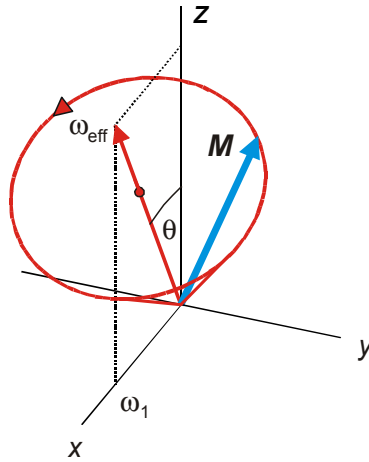
$$\omega_1 = \gamma B_1 \quad (2.14)$$

quantifies the strength of the oscillatory field.

For $|\Omega_0| \gg \omega_1$ (off-resonance irradiation) the spin system is not significantly perturbed. This is because the rotating frame precession with angular frequency Ω_0 averages the effect of the oscillatory field along the x direction. In contrast, for $\Omega_0 = 0$ the precession due to the static field vanishes in the rotating frame and only the oscillatory field drives the motion of the magnetization vector. Hence, the magnetization vector precesses with angular frequency ω_1 about the x axis of the rotating frame. This case corresponds to *resonant irradiation*,

$$\omega_{\text{osc}} = \omega_0 \Rightarrow \Omega_0 = 0 . \quad (2.15)$$

In general, the magnetization vector precesses about an effective field that can be pictured as the vector sum of $\vec{\Omega}_0$ and $\vec{\omega}_1$. The precession cone is tilted by an angle $\theta = \arctan(\omega_1/\Omega_0)$.



1.2 Continuous irradiation

After an irradiation time that is much longer than the longitudinal and transverse relaxation times T_1 and T_2 , the spin ensemble should attain a *steady state*. The magnetization vector in this steady state can be computed from the requirement that the derivatives of its components be zero. From equations (2.11)-(2.13) we find

$$-\Omega_0 M_y - \frac{M_x}{T_2} = 0, \quad (2.16)$$

$$\Omega_0 M_x - \omega_1 M_z - \frac{M_y}{T_2} = 0, \quad (2.17)$$

$$\omega_1 M_y - \frac{M_z - M_0}{T_1} = 0. \quad (2.18)$$

This system of three linear equations can be solved for the three variables M_x , M_y , M_z . We obtain

$$M_x = M_0 \omega_1 \frac{\Omega_0 T_2^2}{1 + \Omega_0^2 T_2^2 + \omega_1^2 T_1 T_2}, \quad (2.19)$$

$$M_y = -M_0 \omega_1 \frac{T_2}{1 + \Omega_0^2 T_2^2 + \omega_1^2 T_1 T_2} , \quad (2.20)$$

$$M_z = M_0 \frac{1 + \Omega_0^2 T_2^2}{1 + \Omega_0^2 T_2^2 + \omega_1^2 T_1 T_2} . \quad (2.21)$$

We first consider the case of resonant irradiation, $\Omega_0 = 0$. The magnetization component with the same phase as the irradiation, M_x , vanishes. The magnetization component that is phase shifted by 90° , M_y , is proportional to the equilibrium magnetization M_0 , and, for

$$\omega_1^2 T_1 T_2 \ll 1 \quad (2.22)$$

is also proportional to the irradiation field strength ω_1 . Thus, M_y corresponds to the absorption signal. The condition expressed in equation (2.22) also ensures that

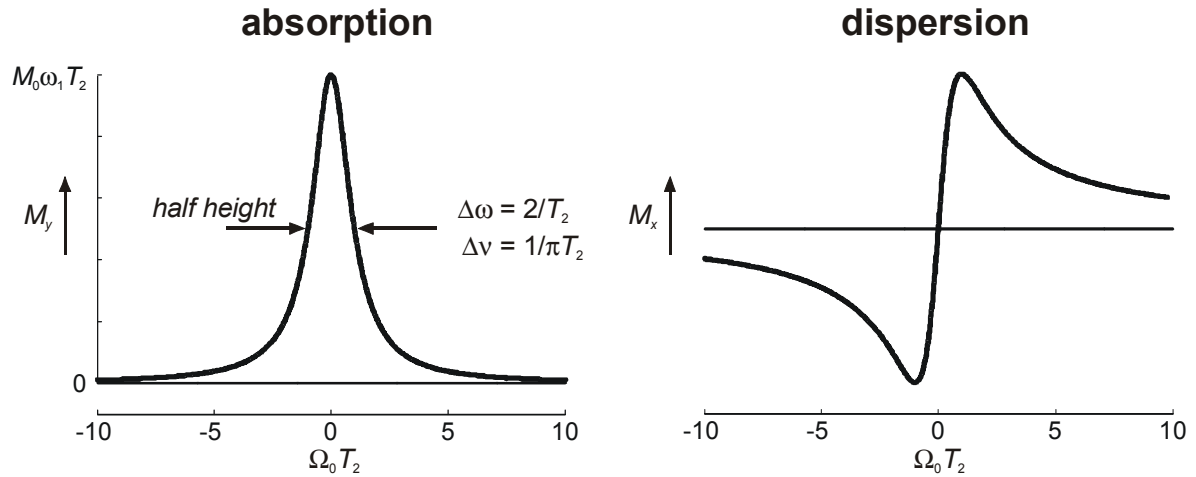
$$M_z \approx M_0 , \quad (2.23)$$

i.e., the spin system is close to equilibrium. If condition (2.22) is violated, the signal M_y grows less than linearly with ω_1 , which is called a *saturation effect*. At sufficiently large irradiation field strengths the signal attains a maximum and if both $\omega_1 T_1 \gg 1$ and $\omega_1 T_2 \gg 1$ are fulfilled, the signal vanishes again!

We now discuss the shapes of the resonance lines corresponding to M_y and M_x , i.e., the dependence of these magnetization vector components on Ω_0 . These shapes do not depend on ω_1 as long as the transition is not saturated, i.e., as long as condition (2.22) is fulfilled. For M_y we find

$$M_y(\Omega_0) = M_0 \omega_1 T_2 \frac{1}{1 + \Omega_0^2 T_2^2} . \quad (2.24)$$

This lineshape is a Lorentzian absorption line with a full width at half height (FWHH) of $2/T_2$. Note that this width corresponds to angular frequencies. On a frequency scale, the width is by a factor of 2π smaller, i.e., the FWHH is $1/(\pi T_2)$.

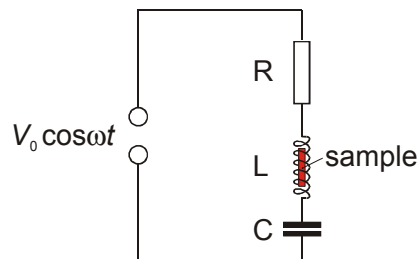


The signal corresponding to M_x vanishes only exactly at resonance. We find

$$M_x(\Omega_0) = M_0 \omega_1 T_2 \frac{\Omega_0 T_2}{1 + \Omega_0^2 T_2^2}, \quad (2.25)$$

which gives the shape of a Lorentzian dispersion line. Note that the dispersion line is much broader. Whenever possible, magnetic resonance experiments are therefore performed in a way that provides pure absorption lines.

1.3 Physics of detection



On resonance or near resonance the sample absorbs part of the irradiation and converts it to heat by spin-lattice relaxation. Due to the small population difference between the two spin levels

this absorption is weak, i.e., only a small part of the total power is absorbed. Such a weak absorption is best measured by detecting the influence of the sample on a resonant circuit.

The frequency of such a circuit is given by

$$\omega_{\text{LC}} = \frac{1}{\sqrt{LC}} . \quad (2.26)$$

It is usually tuned to the radiofrequency (or microwave frequency) of the irradiation. The amplitude of the driven oscillation then depends on the driving amplitude V_0 and the *quality factor*

$$Q = \frac{1}{R} \sqrt{\frac{L}{C}} . \quad (2.27)$$

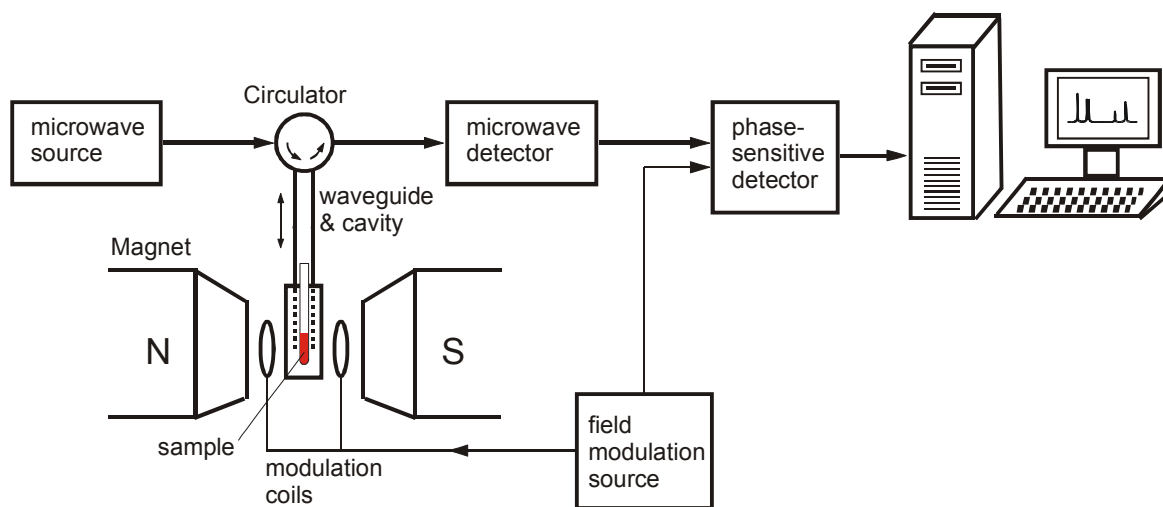
If the spin ensemble is in resonance with the irradiation, there is an additional resistance R_{sample} due to the absorption of the irradiation by the sample. This causes a decrease in the Q value which in turn leads to changes in several characteristics of the RLC resonant circuit. This decrease of the Q value is detected. In combination with a circulator (see below), it is possible to separate the small change from the large total power. Sensitivity of the detection thus increases tremendously.

2 The Continuous Wave EPR Spectrometer

In NMR spectroscopy, continuous wave (CW) techniques have been almost completely superseded by the more versatile and often more sensitive Fourier transform (FT) techniques discussed in lecture 3. The advantage of FT techniques is to some extent due to the narrow dispersion of resonance frequencies of a given isotope in NMR. In such a situation the whole spectrum can be excited by a short irradiation pulse. In EPR spectroscopy, resonance frequencies vary over a much broader range, so that usually only a small part of the spins can be excited by a pulse. CW EPR measurements are thus often more sensitive than pulse measurements. Furthermore, CW EPR is applicable over a broader range of relaxation times and is technically easier to realize, in particular at frequencies larger than 200 GHz. For all these reasons, CW EPR will not be completely superseded by FT EPR or other pulse techniques in the near future.

2.1 The CW EPR Spectrometer

The basic setup for CW EPR consists of a microwave source, a magnet with variable field, a resonant cavity, magnetic field modulation coils, a microwave diode as detector, a phase-sensitive detector, and a computer for data acquisition, storage, and processing. The cavity substitutes for the RLC resonant circuit at microwave frequencies, where conventional coils and capacitors would have impractical dimensions. A cavity is basically an empty metal box with dimensions on the order of the wavelength of the microwave irradiation (~cm to ~mm range).



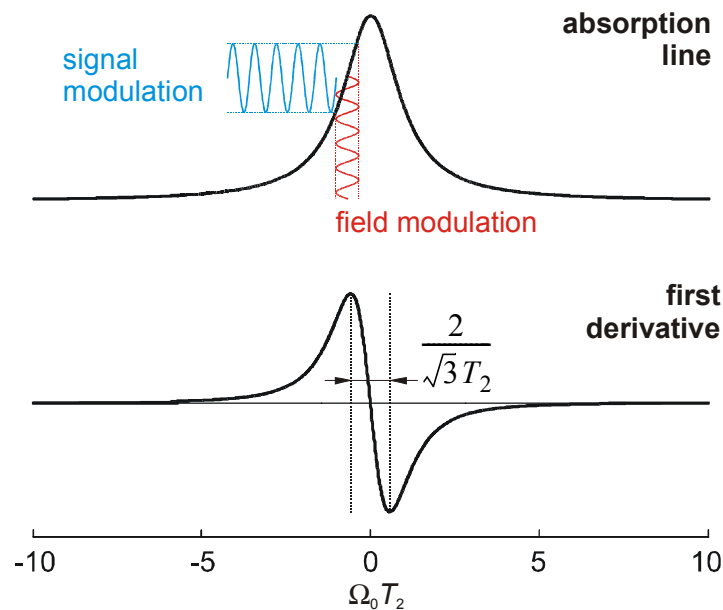
The experiment is done at fixed microwave frequency to avoid retuning of the cavity during the sweep. Instead of the frequency, the magnetic field is swept, which is equivalent as the resonance condition is

$$\nu_0 = \frac{g\mu_B}{h} B_0 . \quad (2.28)$$

At a field where the spin system is off resonance, the cavity is tuned to the microwave frequency and the impedance (complex resistance) of the cavity is matched to the impedance of the waveguide (usually 50 Ω). Under these conditions, no microwave is reflected by the cavity. In other words, all the power that is transmitted from the source to the cavity is absorbed by the resistance R of the resonance circuit. Therefore, no microwave leaves the cavity towards the circulator and no power is transmitted from the circulator towards the microwave detector. When the spin system is brought into resonance by changing the magnetic field, it starts to absorb microwave. Thus, the impedance and Q value of the cavity change. This causes reflection of a

small part of the microwave power. The circulator guides this reflected microwave power towards the detector and a signal arises.

The setup described so far would not be very sensitive as affordable microwave detectors (diodes) are very broadband and therefore gather noise over a broad frequency range. To overcome this problem the magnetic field is modulated at a low frequency (typically 100 kHz). This causes a modulation of the reflected microwave and thus of the detector output current with the same low frequency. The phase sensitive detector basically measures the amplitude of this signal modulation. Since most of the microwave noise does not oscillate at this low frequency and with the same phase as the field modulation, it is suppressed. As a consequence of this kind of detection, changes in the signal are measured that are caused by the field modulation. The signal acquired during the field sweep therefore corresponds to the derivative of the absorption line.



Although the derivative absorption line looks similar as a dispersion line, it is much narrower. In fact, resolution in derivative absorption spectra is significantly better than in pure absorption spectra, while resolution in dispersion spectra is significantly worse.