Physikalischen Fortgeschrittenenpraktikums
an der Universität Konstanz

Nuclear magnetic resonance in the Earth's magnetic field

1 Learning targets

After working on the NMR experiment you will be able to express the fundamentals of nuclear magnetic resonance spectroscopy, manipulate the magnetisation of a sample by the application of appropriate pulse sequences and deduce the underlying relaxation mechanisms from the system's answer.

2 Applications of NMR: what is it good for?

- Structure determination of molecules in chemistry and biology (large organic molecules, proteins)
- Analysis of molecular dynamics (polymer dynamics; water diffusion in drilling cores)
- Imaging (medical NMR tomography)
- Industrial applications (quality control of vulcanised rubber in tires; fat/water ratio in cooking oil, margarine or seeds)

Q1: Name an application where you would use an NMR technique and specify why it is superior to other techniques in this special case.

3 Preparation

After your successful preparation for the experiment you will be able to discuss the MARKED TOPICS during the preexam.

3.1 Nuclear moments and spin dynamics

Most atoms have an ANGULAR MOMENTUM $\vec{L} \neq 0$, depending on their atomic and mass numbers. This nuclear spin is related to a MAGNETIC MOMENT

$$\vec{\mu}_n = \gamma_n \vec{L} = \gamma_n \hbar \vec{I} \tag{1}$$

with the gyromagnetic ratio γ_n of the observed nucleus. From QUANTUM MECHANICAL TREATMENT OF THE ANGULAR MOMENTUM the eigenvalues of $\vec{I}^2$ and I_z are known as I and m.

In an external magnetic field $\vec{B_0} = B_0 \hat{z}$ there are discrete orientations of the nuclear spins relative to the field vector according to the MULTIPLICITY $2I + 1$ of the states. In this NUCLEAR ZEEMAN EFFECT different spin orientations correspond to different energy values

$$E_m = -\vec{\mu}_n \cdot \vec{B}_0 = -m\gamma_n \hbar B_0. \tag{2}$$

In thermal equilibrium the different states are occupied according to BOLTZMANN'S STATISTICS with a propability

$$P(m) \propto \exp\left(-\frac{-m\gamma\hbar B_0}{k_B T}\right) \tag{3}$$

> Q2: How large is the Zeeman energy splitting for a magnetic flux of $B = 5$ T in a typical NMR experiment and in the Earth's magnetic field of $B \approx 50$ µT? What are your experiences with the frequencies of the electromagnetic radiation which stimulates transitions between these Zeeman levels?

The NET MAGNETISATION $\vec{M}$ of a sample containing N atoms is N times the expectation value of the magnetic moment $\langle \mu_n \rangle$:

$$M = \frac{\chi_0}{\mu_0} \cdot B_0 \text{ with } \chi_0 = N\gamma\hbar \frac{\sum\limits_{m=-I}^{I} m \exp(m\gamma\hbar B_0/k_B T)}{\sum\limits_{m=-I}^{I} \exp(m\gamma\hbar B_0/k_B T)}. \tag{4}$$

In NMR the exponent is usually small and can therefore be expanded linearly which results in the DERIVATION OF CURIE'S LAW

$$M \approx \frac{N\gamma^2\hbar^2 I(I+1)}{3k_B T} \cdot \frac{B_0}{\mu_0}. \tag{5}$$

A magnetic moment μ in a magnetic field B feels a torque which changes the angular momentum L and therefore also the magnetic moment μ:

$$\frac{d\mu}{dt} = \gamma_n \vec{\mu} \times \vec{B} \tag{6}$$

Since μ_n is not collinear to B_0 it PRECESSES with the LARMOR FREQUENCY

$$\vec{\omega}_0 = -\gamma_n \vec{B}_0 \tag{7}$$

around the magnetic field vector. An ensemble of magnetic moments is equally distributed on the surface of two equal cones with rotational symmetry around the $\vec{B}_0$ axis. The z components of these magnetic moments add to the net magnetisation M while the x and y components of the moments opposing each other on the cone cancel. In a ROTATING COORDINATE SYSTEM $\{x', y', z\}$ spinning with the Larmor frequency, M is static and B_0 VANISHES.

An magnetic field $\vec{B}_1$ perpendicular to $\vec{B}_0$ in the laboratory frame and oscillating at the Larmor frequency ω_0 has ONE COMPONENT WHICH IS STATIC IN THE ROTATING COORDINATE FRAME. Therefore in the rotating frame the magnetic moment precesses around $\vec{B}_1$ with the angular velocity

$$\omega_1 = -\gamma_n B_1. \tag{8}$$

Applying a $90°$ PULSE by switching on the magnetic field B_1 for a pulse duration of $0.25 \cdot \tau_1 = 0.25 \cdot 2\pi/\omega_1$ rotates the magnetic moment by $90°$ into the x'y' plane. Doubling either the pulse duration or the field would rotate the magnetic moment by $180°$, thus leading to an $180°$ PULSE. After the perturbation of the spin by a $90°_x$ pulse along the x' axis the net magnetisation lays along y'. After switching off the transversal B_1 field the net magnetisation exponentially relaxes with the time constant T_1 back into the state with MINIMAL FREE ENERGY parallel to B_0. This realignment *along* B_0 is called LONGITUDINAL RELAXATION or SPIN-LATTICE RELAXATION, since the energy in the spin system due to the $90°$ pulse is distributed over the surrounding medium by DIPOLE-DIPOLE INTERACTIONS.

After a $90°$ pulse along x' the individual magnetic moments are arranged around the y' and the $-y'$ axis. But this PHASE COHERENCE decreases since the individual moments precess at different angular velocities around the direction of $\vec{B}_0$ due to local magnetic fields $B_0 + \Delta B(\vec{r})$. Some moments go faster than ω_0, some lag behind and the distribution of the spins fans out. This process in the plane transversal to B_0 is called TRANSVERSAL RELAXATION. Another mechanism for phase decoherence in the transversal plane is the SPIN-SPIN RELAXATION, where two spins exchange their states (spin flip). The ENTHALPY is conserved while the ENTROPY of the system increases. The relaxation is described by the time constants T_2^* and T_2:

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \gamma \Delta B(\vec{r}) \tag{9}$$

A quantitative description of the physical mechanisms behind relaxation is quite ambigious. The Bloch formalism makes an empirical approach and *assumes* an exponential decay for the magnitude of the magnetisation along different the z and the x', y' axes. This is subsumed in the BLOCH EQUATIONS.

3.2 Earth's magnetic field and prepolarisation

The nuclear magnetic resonance experiments will be conducted in the EARTH'S MAGNETIC FIELD B_0. It is characterised by its FLUX DENSITY, INCLINATION, DECLINATION, THE HIGH HOMOGENEITY AND TEMPORAL FLUCTUATIONS. The equilibrium magnetisation M is induced by a less homogeneous but 350 times stronger polarisation magnetic field B_p perpendicular to B_0. After switching off B_p M aligns along B_0.

3.3 Signal acquisition and experimental details

The signal aquired in an NMR experiment is the sinusoidal voltage induced by the precessing transversal magnetisation in a coil (B_1 coil) located along the x axis. The amplitude of this voltage decreases due to relaxation effects which is called the FREE INDUCTION DECAY. The B_1 coil in conjunction with an external capacitance forms a RESONANT RLC CIRCUIT tuned to the Larmor frequency.

Since we are interested in the resonance frequencies of the sample we have to transform the induced sinusoidal voltage from time domain to the frequency domain by means of the FOURIER TRANSFORM. A very long sinusoidal signal would result in an extremely sharp spectral line, but due to the above mentioned relaxation processes, the oscillation is exponentially damped. This results in a LORENTZIAN LINE SHAPE as can be deduced from the FOURIER TRANSFORMATION OF AN EXPONETIALLY DAMPED SINUSOIDAL OSCILLATION.

Although the Earth's magnetic field is very homogeneous local variations due to para- or ferromagnetic objects close to the coil have to be compensated by SHIMMING of the measurement field B_0.

3.4 Longitudinal relaxation measurements

The INVERSION-RECOVERY PULSE SEQUENCE is used to measure the transversal relaxation time T_1 by aligning M antiparallel to B_0 by a 180° pulse, let M relax towards B_0 and then probing the recovered magnetisation by a 90° pulse. In a large magnetic field (≤ 0.5 T) one observes the zero crossing of the magnetisation. In contrast in Earth's magnetic field the final equilibrium magnetisation is already close to zero so the magnetisation in fact relaxes against zero with T_1 and no zero crossing is observed. During your experiment T_1 is measured in the polarising field B_p and in the Earth's magnetic field B_0. In the first case the polarizing field is applied for an interval τ_p and the resulting magnetisation is probed with a 90° pulse. In the second case a constant magnetisation is produced by a polarising pulse of constant length and the decay of $\vec{M}$ is probed after a delay τ_1 with a 90° pulse.

3.5 Transversal relaxation measurements

The dephasing of the transversal magnetisation due to inhomogeneities of B_0 can be reversed by a HAHN OR SPIN ECHO pulse sequence. A $90°_{x'}$ pulse aligns the magnetisation along the y' axis. Then the ensemble fans out since the spins in higher fields run ahead of the ensemble while the nuclei in the regions with lower B_0 lag behind. When we now apply a $180°_{y'}$ pulse after a time τ_E the order of the spins within the ensemble is reversed. The fast spins originally at the front of the ensemble now are at its end and start to catch up. The slowly precessing spins are at the front now but will be overtaken soon by the faster spins behind them. Nearly all spins meet up after the rephasing time τ_E and the temporal signal shows a maximum, called the spin echo. The effect of the spin-spin interaction is not reversible, therefor the echo signal is not as high as the original signal. This decay in the maximal amplitude is used to measure the spin-spin relaxation time T_2 by varying the echo time τ_E in multiple spin echo experiments. Single-shot T_2 measurements can be achieved by multiple-echo pulse sequences like the Carr-Purcell and the Carr-Purcell-Meiboom-Gill (CPMG) sequence.

4 Experiments

A good preparation for the actual experiment is a measurment schedule. Think in advance what are the important characteristics for the reconstruction of your measurements and what data do you need for the analysis of these measurements. The experiments proposed in the following section are suggestions but not necessarily complete!

1. The coil is analysed by its ring-down after a B_1 pulse. In an NMR experiment the coil's resonance frequency is tuned to ω_0 by a capacitance inside the control unit. Acquire an adequate calibration curve for this purpose! How would you describe the cavity ring down spectrum?

2. Find an appropriate location for the coil assembly with a noise level below 10 µV and a ^{1}H Larmor frequency ω_0 within the tuning range of the capacitance!

3. Check that the coil's resonance frequency is tuned to the ^{1}H Larmor frequency ω_0 by monitoring the ^{1}H signal of the tap water sample on top of the cavity ring-down.

4. Find the optimal B_1 lengths for the 90° and 180° pulses.

5. By shimming you optimise the B_0 homogeneity and therefore the Signal-to-Noise ratio (SNR). Adjust the shim gradients in the PulseAndCollect experiment for an optimised signal amplitude of the ^{1}H line. Document your success!

6. Spin-lattice (longitudinal) relaxation. What is the difference in the T_1 relaxation for the ^1H signal in tap water and in cooking oil[1]? Compare your measured times and discuss the results!

7. Spin-spin (transversal) relaxation: Compare the values of T_2 for tap water measured by the Hahn echo, the CP and the CPMG sequence. Investigate the relation described by equation 9.

[1] For the preparation of the oil sample you can bring approx. 500 ml of your favourite cooking oil.

8. Paramagnetic Cu^{2+} ions influence the relaxation times of water protons. Investigate this influence by appropriate mesurements on four samples with different concentrations of copper sulfate ($CuSO_4$). Discuss your results!

5 Literature suggestions

- Macomber, R. S., *A complete introduction to modern NMR spectroscopy*, John Wiley & Sons, New York, 1998.
- Derome, A. E., *Modern NMR Techniques for Chemistry Research*, Pergamon Press, Oxford, 1987.
- Carrington, A., McLachlan, A. D., *Introduction to Nuclear Magnetic Resonance*, Chapman and Hall, London, 1979.