Nuclear Magnetic Resonance

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Revision History

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Contents

1 Theory

1.1 Introduction

Due to the magnetic moment of atomic nuclei, energy splitting occurs in the presence of an external magnetic field. If the nuclei are additionally irradiated with photons of the correct energy (electromagnetic radiation in the range from 4 to 600 MHz), they can pass from energetically lower states to higher states through absorption of these photons. Such a flipping of the spin occurs in both simple and complex nuclei and is referred to as nuclear magnetic resonance. Nuclear Magnetic Resonance spectroscopy (NMR) is based on the measurement of this energy absorption and is now one of the most important methods for studying the structures of organic and inorganic substances.

The theory for NMR goes back to W. Pauli (1924), who suggested that certain atomic nuclei have a spin and a magnetic moment and that these properties lead to a splitting of their energy levels in a magnetic field. In the following decade these postulates could be confirmed experimentally. But

it was not until 1946 that Bloch and Purcell succeeded in proving independently of one another that atomic nuclei in a strong magnetic field absorb electromagnetic radiation as a result of the splitting of their energy levels produced by this field. In the first five years after the discovery of nuclear magnetic resonance, chemists found out that the molecular environment influences the absorption of radiation in the high frequency range caused by a nucleus in the magnetic field and that this effect allows conclusions to be drawn about the molecular structure.

The following theoretical part of these instructions is intended to facilitate an entry into the specialized literature (see Bibliography, page 14), but does not replace it.

1.2 Spin, magnetic moment

1.2.1 Analogy: electron with orbital angular momentum

Electrons with orbital angular momentum $\vec{L}$ form a circular current and thus an atomic magnetic dipole. A discrete spectrum of the energy states of a dipole in the magnetic field is linked to the discrete spectrum of the angular momentum states. The dipole moment is proportional to the circular current and the area enclosed by it. An electron with angular momentum $\vec{L}$

$$\vec{L} = m_e \cdot R^2 \cdot \vec{w} \tag{1}$$

forms a magnetic dipole with dipole moment $\vec{\mu}$

$$\vec{\mu} = I \cdot \vec{A} = \frac{-e\,w}{2\pi} \cdot R^2 \cdot \pi \cdot \frac{\vec{w}}{|\vec{w}|} = \frac{-e\,\vec{L}}{2m_e} = -\mu_B \frac{\vec{L}}{\hbar} = \gamma \cdot \vec{L} \tag{2}$$

where μ_B is Bohr's magneton ($\mu_B = \frac{e\hbar}{2\,m_e}$). The proportionality factor γ, of $\vec{\mu}$ and $\vec{L}$, is called the gyromagnetic ratio. For electrons the following applies: $\gamma = -\mu_B \hbar$.

The amount and (e.g.) the third component of the angular momentum form a complete set of interchangeable observables (apart from the spin) for a fixed energy eigenvalue n in its eigenspace. Their spectrum of eigenvalues is discrete and is usually written as follows

$$\vec{L^2} = \hbar^2 \cdot \ell \cdot (\ell + 1), \qquad \ell = 0, 1, \ldots, n \tag{3}$$
$$L_3 = \hbar \cdot m, \qquad m = -\ell, -\ell + 1, \ldots, \ell \tag{4}$$

The same applies to the magnetic moment:

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$$\vec{\mu}^2 = \gamma^2 \cdot \hbar^2 \cdot \ell \cdot (\ell+1) = \mu_B^2 \cdot \ell \cdot (\ell+1), \qquad \ell = 0, 1, \ldots, n \qquad (5)$$

$$\mu_3 = \gamma \cdot \hbar \cdot m = -\mu_B \cdot m, \qquad\qquad m = -\ell, -\ell+1, \ldots, \ell \qquad (6)$$

The force on a magnetic dipole in a homogeneous magnetic field $\vec{B} = (0, 0, B)$ is zero for reasons of symmetry. On the other hand, the torque acting on it does not vanish, but is $\vec{M} = \vec{\mu} \times \vec{B}$. The torque makes the dipole move with the frequency $\omega = \gamma \cdot B$ around the axis $\vec{B}$ ($L_3 = 0$). The potential energy of the dipole depends only on its orientation in the field:

$$U = -\vec{\mu} \cdot \vec{B} = -\mu_3 \cdot B = \mu_B \cdot B \cdot m, \quad m = -\ell, -\ell+1, \ldots, \ell \qquad (7)$$

So there are $2 + 1$ states. The energy difference between two adjacent energy states is:

$$\Delta U = \mu_B \cdot B = -\gamma \cdot B \cdot \hbar = -\omega \cdot \hbar \qquad (8)$$

Here ω corresponds to the precession frequency. This is also called transition frequency or Larmor frequency.

1.2.2 Atomic Nuclei with Spin

The spin of an atomic nucleus also has a magnetic moment attached to it:

$$\vec{\mu} = \gamma \cdot \vec{s} \qquad (9)$$

$$\vec{\mu}^2 = \gamma^2 \cdot \hbar^2 \cdot s \cdot (s+1), \quad s \text{ depends on the nucleus } \left(0, \frac{1}{2}, 1, \ldots\right) \qquad (10)$$

$$\mu_3 = \gamma \cdot \hbar \cdot m_s, \qquad\qquad m = -s, -s+1, \ldots, +s \qquad (11)$$

In the remainder of this paper, we will only consider kernels with $s = \frac{1}{2}$. γ is still called the gyromagnetic ratio, but in the case of coupling to a spin it can only be predicted relativistically. γ is nucleus specific and can be positive or negative (moment parallel or antiparallel to the spin). The potential energy in the homogeneous magnetic field is:

$$U = -\vec{\mu} \cdot \vec{B} = -\mu_3 \cdot B = -\gamma \cdot \hbar \cdot B \cdot m_s \qquad (12)$$

and the difference of two adjacent levels

$$|\Delta U| = |\gamma| \cdot \hbar \cdot B = |\vec{\omega_0}| \cdot \hbar \qquad (13)$$

Also the spin precesses around the B-axis with the frequency

$$\vec{\omega_0} = -|\gamma| \cdot \vec{B} \qquad (14)$$

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1.3 Spin Resonance.

If an alternating field $\vec{B}_1 = (B_1 - cos(\omega_1 t), 0, 0)$ is superimposed on the homogeneous field $\vec{B}_0 = (0, 0, B0)$ ($B_1 << B_0$), transitions between spin states can be excited at a suitable frequency ω_1. This occurs with probability significantly different from zero only if the frequency corresponds to the energy difference of the states under consideration, i.e.

$$\omega_1 = \omega_0 = |\gamma| \cdot B_0 \tag{15}$$

This situation is called resonance.

1.4 Spin system.

In a set of N magnetic dipoles in thermal equilibrium, the distribution of the dipoles among the different energy levels is given by the Boltzmann distribution. The expectation value $< N_i >$ of the number of dipoles in the state with energy E_i is

$$< N_i > = \frac{N}{Z} \cdot e^{-E_i/kT} \tag{16}$$

$$Z = \sum_i e^{-E_i/kT} \tag{17}$$

Transferred to the model of spin-$\frac{1}{2}$-particles, this expectation value becomes

$$< N_\pm > = \frac{N}{Z} \cdot e^{\vec{\mu}\vec{B}_0/kT} \approx \frac{N}{Z} \cdot \left(1 \pm \frac{\mu_3 B_0}{kT} \right) \tag{18}$$

"+" stands for μ parallel to $\vec{B}_0$, "-" for μ antiparallel to $\vec{B}_0$. The former is the energetically lower state. The approximation for $< N_\pm >$ is admissible and good due to $\frac{\mu_3 B_0}{kT} \approx 10^{-6}$. (For the proton, μ also makes s parallel or antiparallel to B_0, since γ is positive. In contrast for the electron or neutron γ is negative).
The spin overshoot, by which the total magnetic moment is determined, is as follows

$$< \Delta N > = < N_+ - N_- > \approx N \cdot \frac{\mu_3 B_0}{kT} \tag{19}$$

With the alternating field B_1 switched on, transitions between the two levels are excited, and the spin overshoot may be shifted.
Because of the larger number of spins in the energetically lower level, a net energy absorption from the alternating field occurs first. This absorption

increases the spin temperature, i.e. the spin excess decreases and the occupation numbers equalize. The spin system is saturated in this case, no net absorption takes place anymore. This effect is counteracted by a recovery of the system. Over the remaining degrees of freedom of the sample, the spin system tries to release its excess energy after each excitation. The faster the recovery, the larger the possible new excitation. Because the atomic nuclei in the molecule are relatively isolated and have little opportunity to interact with the environment, the usual recovery times (also called relaxation times) are very large (10^{-4} to 102 s) compared to other nuclear processes. By adding paramagnetic ions to the sample (in our case it will be Fe^{3+} ions) the spin lattice and spin-spin coupling can be intensified and the recovery times can be shortened.

1.5   Relaxation.

In the literature, relaxation effects are divided into two classes. For both, an exponential recovery is assumed.

1.5.1   Spin-Lattice relaxation.

The absorbing nuclei in an NMR experiment are part of a larger set of atoms that make up a sample. The total set is called a lattice, regardless of whether it is a solid, a liquid or a gas. Oscillations and rotational motions of the nuclei lead to a complex magnetic field in the vicinity of each nucleus and thus to a coupling between the individual nucleus and the lattice. The energetic recovery of a system due to this spin-lattice interaction is called longitudinal or thermal recovery. This is characterized by the relaxation time T_1. In the absence of the alternating field, T_1 is defined by the equation

$$\dot{M}_z = -\frac{M_z - M_0}{T_1} \tag{20}$$

where M_z is the magnetization of the sample in the direction of $\vec{B}_0$ and M_0 is the equilibrium value of the magnetization in the $\vec{B}_0$ field ($M_0 = \chi - H_0, \chi :$ *susceptibility*).

T_1 depends strongly on the mobility of the lattice. For solids and viscous fluids, the lattice is relatively immobile, and T_1 is accordingly large. In contrast, for gases the mobility of the lattice is large and thus T_1 is very short.

1.5.2 Spin-spin relaxation.

The recovery due to spin-spin interaction is called transverse recovery. It describes the smearing of the coherence of the precessing spins and is characterized by the relaxation time T_2, where valid.

$$\dot{M}_x = -\frac{M_x}{T_2}, \quad \dot{M}_y = -\frac{M_y}{T_2} \tag{21}$$

M_x and M_y are the magnetizations of the sample in the direction of the first and second space dimension. For many liquids, the values for T_1 and T_2 are approximately the same. In contrast, the spin-spin relaxation times T_2 of crystalline solids and viscous fluids are very small (up to 10^{-4} s).

1.6 Pulse technique.

In contrast to continuous excitation as used by the pioneers of nuclear magnetic resonance (cf. historical publications in the ring binder [6]), NMR instruments today are usually operated in pulsed mode. For the technique, advantages, and applications of the various pulsed methods, please refer to the literature, in particular to the book "Principles of Magnetic Resonance" [1] (p. 39-45 and p. 367-369) and the instrument manual [10].

2 Tasks.

1. A sound qualitative understanding of the theory is of great importance for this experiment. In addition to the theory in chapter 1 of this tutorial, you will find in the manual of the TeachSpin PS1-A [10] under the heading "Introduction" a part of the theory that is oriented towards the NMR experiments to be performed here. We also recommend a well understandable theory, which is available on the web and supplemented with many illustrative pictures (http://www.cis.rit.edu/htbooks/nmr [11]). Very theoretical but complete and therefore helpful is the book "Principles of Magnetic Resonance" [1]. Further literature references can be found in the bibliography on page 14. Work carefully into the NMR theory.

2. In the manual for the TeachSpin PS1-A you will find an introduction to the most important components of the available NMR instrument under the heading "The Instrument". It describes how the instrument works and what the various components and parameters mean. Work

through the introduction to get an idea of the setup of the experiment and return to this section later if you have any problems.

3. For the measurement of the relaxation times T_1 and T_2, it is important that the parameters are optimally set. In the manual under the heading "Getting Started" you will learn the technique by means of small introductory experiments. To perform these experiments you will need the Tektronix oscilloscope. The oscilloscope is triggered externally by the TeachSpin electronics (Sync Out). Information about the oscilloscope can be found in the corresponding manual. Perform experiments A to D and F to H (without self-diffusion). From experiment D on, use the sealed sample tube with mineral oil as a sample. Note that the black O-ring on the tube can be used to adjust the high position in the magnet. The high position has an influence on the amplitude of the signal to be measured. Therefore, the signal must always be optimized to the maximum amplitude during a measurement.

4. Now carry out experiment E. As described in the instructions on page 31, the position of the sample in the magnet can be adjusted by two threaded spindles. This allows the "sweet spot" to be found. Plot the magnetic field as a function of the two position axes in a contour plot. Assess whether it is possible to record a spectrum (Fourier transform of the FID signal) of e.g. ethanol (C_2H_5OH) despite the inhomogeneity of the magnetic field? Information and theory about spectra can be found in [5].

5. Determine the relaxation times T_1 and T_2 on four samples with different Fe-ion concentrations. The mixing ratios should be 100 ml distilled water at 1000 mg, 100 mg, 10 mg and 0 mg $Fe(NO_3)_3 \cdot 9H_2O$. Empty sample tubes and a packed and weighed quantity of $Fe(NO_3)_3 \cdot 9H_2O$ (approx. 100 mg) are available for this purpose. To determine the relaxation times, it is important that the Fe ions in the dest water are well dissolved. Therefore, mix the samples in the available vessels and do not pour the solutions into the sample tubes until the powder has dissolved. Measurements with large T_1 or T_2 are experimentally more demanding. Therefore, start with the sample that has the highest Fe ion concentration. Choose the measurement method for T_1 or T_2 which seems to be the most reasonable. Sample tubes must not show residues of the Fe solution before or after the experiment. Therefore, rinse the sample tubes well with distilled water before and after the experiment and never let the Fe solution dry up.

6. The FID signal can be used as a measure of the number of excitable nuclei. Assume the water content of corn grits from the comparison with distilled water. If the water content in the corn grits is determined by the presence of the H-kernels outside the Water (e.g. in carbohydrates), can it be overestimated? To check this, a measurement must be carried out with dried maize semolina. The maize semolina is heated in a spoon over a flame. Check the estimated water content by weighing the corn before and after drying.

7. Virtually all biological materials contain water, which can be measured with the available spectrometer. Select some of the materials and comment on the measured relaxation times.

8. All self-filled sample tubes and the used sample vessels and tools must be cleaned thoroughly with distilled water after the experiments.

3 Devices and material.

3.1 Material in the lab

1. TeachSpin PS1-A NMR spectrometer with permanent magnet.

2. 7 BNC cables blue of different length.

3. 1 BNC T-piece.

4. 1 BNC termination 50W.

5. 1 dummy signal coil.

6. 1 pickup sample.

7. 1 Manual for the spectrometer (red folder).

8. Tektronix Oscilloscope TDS 200 with manual.

9. 2 oscillator probes.

10. Pentium PC with Tektronix software for data acquisition via RS 232.

11. 1 measuring cylinder (glass).

12. 1 glass pipette large.

13. Plastic pipettes small.

14. Plastic container, cleaned.

15. Various empty sample tubes with lid and O-ring, cleaned.

16. Opener and lighter.

3.2 Software

On the lab computer a measuring software for the Tektronix oscilloscope is installed. The software allows a realtime recording of the measured data. The communication between oscilloscope and software is ensured by a serial interface (RS 232). For further information please refer to the software manual.

3.3 Samples.

1. Sample tube with mineral oil.

2. 1 sample tube with glycerine.

3. 100 mg $Fe(NO_3)_3 \cdot 9H_2O$ packed and weighed.

4. Maize grits packed.

5. Dest'water, alcohol (94%).

4 References

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