Frontiers of NMR in Pulsed High Field Magnets

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Nuclear Magnetic Resonance (NMR) [1,2], originally envisioned for the study of nuclear properties, soon became a very versatile tool for many disciplines. Today, it expands most rapidly in medicine for imaging purposes, but it is advancing deeper into physics, chemistry and biology as a spectroscopic tool as well. The great versatility of NMR is based on the fact that in most materials at temperatures of interest, the nuclear spin states are nearly degenerate and long lived. If this degeneracy is lifted by external or internal fields, nuclear spin transitions can be studied in great detail. The nuclear spin transition frequencies and the nuclear spin dynamics carry a wealth of information about the electronic surrounding of particular nuclei, as well as the properties of the material as a whole. One can study the orbital and spin structure of the electrons (NMR shift analysis), interatomic distances (internuclear coupling analysis), or material density variations (NMR imaging), but also dynamical properties such as low-energy electronic excitations or molecular motion.

The comparably weak coupling of the nuclei through magnetic dipole or electric quadrupole moments to their environments is responsible for the poor signal strength in NMR experiments (e.g., the nuclear Boltzmann factor at room temperature is typically on the order of 10^{-5}). This is a reason why strong magnetic fields are so beneficial for NMR: The higher the magnetic field, the larger is the splitting of the nuclear states. The resulting increase in the resonance frequency not only produces a stronger NMR signal (higher sensitivity), it also increases the resolution since the difference in frequency for two nuclei in a similar but not identical electronic environment increases as well. High fields boost sensitivity and resolution. Apart from the study of the temperature dependence of electronic properties, their response to an external magnetic field of varying strength has been very helpful in elucidating new states of matter especially in physics applications. This is in particularly true for NMR experiments and represents another very important reason why high magnetic fields are of such importance.

Clearly, the magnetic field should also be spatially homogeneous since the spread of nuclear transition frequencies due to the field's spatial inhomogeneity across the sample will limit resolution. Moreover, the field should be stable during the observation of the NMR signal since a variation of the resonance frequency in time can also limit the resolution. It is therefore not surprising that much of NMR's success is based on superconducting magnet technology. Operated in persistent mode, these magnets have a great stability and can be made very homogeneous (e.g., by using long superconducting solenoids aided by superconducting shim coils).

Unfortunately, superconductivity is at odds with high magnetic fields, and today, it seems to be impossible to increase the magnetic field strength with persistent superconducting magnets beyond some 22 Tesla (or frequencies in excess of 1 GHz for ^{1}H NMR [3]). On the other hand, resistive magnets (e.g., based on non-superconducting Cu metal coils) are not subjected to these constraints and can be used to achieve much higher fields [4]. However, they convert a substantial part of the supplied electrical energy to heat, the most serious problem for such magnets. Cooling systems for these coils increase the coil's volume and with it the stored energy that in turn increases the losses. As a consequence, their use for creating high magnetic fields approaches a limit at about 33 Tesla (with tremendous operating costs for electrical energy and cooling procedures). Recently, hybrids of superconducting and resistive magnets [5] have been built to increase the field strength even further, up to 45 Tesla. However, all these systems are very expensive and have a poorer stability and homogeneity compared to superconducting magnets operated in persistent mode.

A comparably inexpensive route to reach much higher fields was introduced by Kapitza [6] long ago. He created pulsed magnetic fields with small coils that are allowed to heat up adiabatically during the pulse. Consequently, small amounts of energy suffice to create very high fields. Due to the rising interest in the generation of high magnetic

fields for condensed matter physics studies, such pulsed field sources have been further developed over the past decade. Peak fields up to 75 Tesla with some 10 ms rise time are available. Here, the mechanical stability of the coil is a limiting factor, but research into new materials may enable us to have 100 Tesla available for some milliseconds in near future, during which physical properties such as resistivity, magnetization and specific heat can be measured. Much higher fields can be created with a destructive single turn coil for several microseconds. The new "High-Field Laboratory Dresden" [7] aims at creating fields up to 100 Tesla during some milliseconds in near future with non-destructive coils.

One may be inclined to think that pulsed magnets are rather ill suited for NMR experiments even if the pulse lengths would be sufficiently long for the observation of NMR (some milliseconds): First, the field is strongly time-dependent and not very well known. Second, since the magnet coils are relatively small, the field has poor spatial homogeneity. Third, one expects the reproducibility of the field to be poor and interrupted from shot to shot by prolonged time periods (in excess of 30 minutes) for cooling of the magnet coil, such that the commonly used NMR technique of signal averaging will be impractical. And indeed, various attempts to perform NMR in such magnets have failed. Nevertheless, given the great potential NMR would have at much higher fields, and with a 60 Tesla pulsed magnet in operation at the IFW-Dresden [8], and a 100 Tesla source under construction, we found it challenging to explore the possibility of performing NMR in greater detail. Figure 1 shows the basic experiment.

Our estimates showed that a small sample size, if it could be facilitated by a sensitive NMR probe, should provide a reasonable homogeneity that, together with the higher sensitivity from the high field, would make NMR interesting for various systems. For our first experiments we chose diluted Cu metal powder as the sample material. Cu has two similarly abundant, NMR-active isotopes (^{63,65}Cu) with similar resonance frequencies that can serve as a test for a "real" signal. In addition, the Fermi contact interaction in the metal shortens the lifetime of the nuclear levels (fast relaxation) such that the nuclei polarize easily at around room temperature during the rise-time of the field. An initial field strength of only 12 T was chosen since

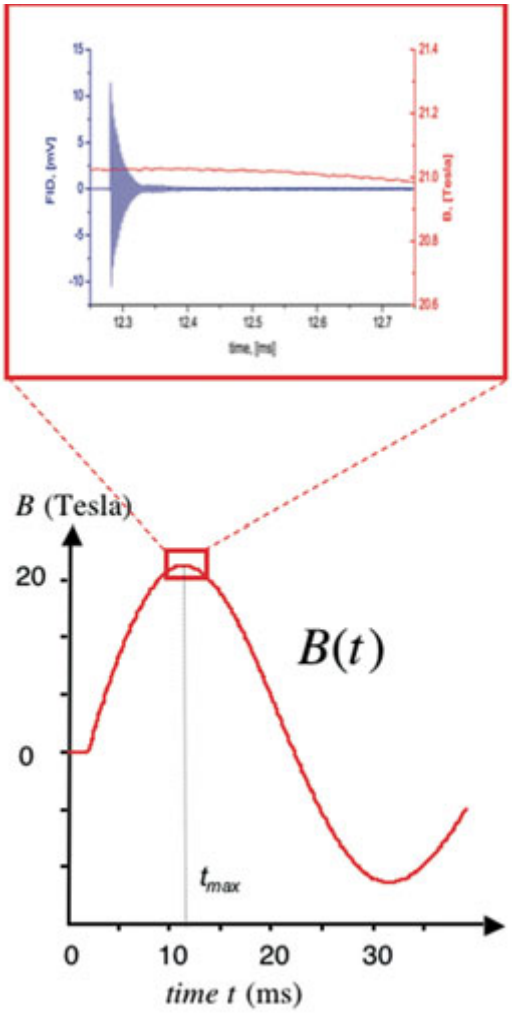

Fig. 1: The lower panel shows a typical time dependence of a field pulse, from measurements with a pick-up coil near the center of the magnet coil. At, a trigger initiates the closing of the switch that connects the capacitor bank with the magnet coil. After a short delay the field in the magnet rises and crests at. Near, a radio frequency pulse of 500 ns duration (250 W) and with a carrier frequency close to the expected nuclear resonance is sent to the NMR probe that is located in the center of the magnet. After the pulse the receiver of the NMR spectrometer that is now connected to the probe is gated on, and a decaying voltage (free induction decay, FID) can be recorded. The upper panel show such an FID after the carrier frequency has been subtracted, together with the actual field trace.

it could be reached with static magnets already present in the laboratory, to facilitate extensive testing in the static field. The resonance frequencies of the Cu isotopes at 12 Tesla are between 135 to 145 MHz. Such low NMR frequencies are easy to handle, just as a receiver bandwidth of a couple of MHz, so that our search window was in excess of 1 % of the target field value. Quite some effort

went into the design of suitable NMR probe systems since the spatial constraints (the probe's outer diameter had to be less than 6 mm) did not leave much room for constructing resonance circuits that can be tuned and matched and are not influenced by the strong field pulse. With a first operating probe and a simple, home-built spectrometer and multi-pulse excitation schemes we began searching for the signal close to the expected occurrence of the field maximum. After some attempts we were successful and could observe the Cu NMR signals [9,10]. These enabled us to improve the positioning, the probe and the calibration of the magnetic field. The measured sensitivity (signal-to-noise) could be accounted for and the resolution was near the value predicted for the sample (that fit a 2 mm outer diameter radio frequency (RF) solenoid of 3 mm length) with the inhomogeneity caused by the quadratic gradients from the magnet coil. These first results were very encouraging, specifically since the resolution was already better than that given by the Cu Knight shifts.

The next challenge was to perform NMR at field strengths in excess of those that could be reached by static magnets available to us (some 15 Tesla), but were necessary to perform reliable tests of the NMR system prior to the pulsed field experiments. We explain below why it was convenient to use a new sample materials that had two isotopes with very different gyromagnetic constants γ, unlike Cu. After some trials with Rb metal we decided to prepare special mixtures of ^1H_2O and ^2H_2O water. The nuclear relaxation was shortened by adding $GdBr_3$ or $GdCl_3$ such that both isotopes could be polarized during the short field pulse. The ratio of the gyromagnetic constants for ^1H and ^2H, $^1\gamma/^2\gamma$ = 6.514403, is known with high precision and does not suffer from unknown shifts between different nuclei. For example, with such samples we could observe the ^1H NMR at 360 MHz at about 9.210 Tesla, while knowing with certainty that the ^2H NMR signal at the same frequency had to occur at a field of 60.000 Tesla. Thus, probe and spectrometer could be tested in a static field with ^1H NMR at a frequency that is subsequently used in the high pulsed field for its calibration. The calibration is necessary since the exact occurrence of the field maximum at $t = t_{max}$ depends on the field strength itself due to a field dependent performance of the magnet coil. Using this scheme we were able to record ^2H NMR at up to 58 Tesla [11]. By also resorting to smaller samples we could increase the resolution until it appeared to be limited by the time dependence of the field pulse. The rapid change of the field during the presence of the signal, i.e., during the time of the coherent nuclear precession, modulates the nuclear precession frequency and creates broadening of the signal in the frequency domain. In an ensuing set of experiments we measured the field's time dependence through pick-up coils with high precision and recorded NMR signals, deliberately beginning at different positions in time t_s, $B(t_s–T_{max})$ with respect to the occurrence of the field maximum at, in order to vary the extend of the distortions (they are expected to be much larger if recorded further away from the maximum where the field changes more rapidly). Since the data acquisition noise in the field vs. time traces was rather large for NMR purposes, we approximated this curve near the maximum by a quadratic function, thereby eliminating most of the noise. This noiseless field dependence was then used to numerically demodulate the different NMR signals. This procedure removed all the distortions from the NMR lines. These were extremely encouraging results as they proved that the field's intrinsic time dependence does not limit resolution [11] (see also Fig. 2 for examples).

These new experiments, which proved that NMR is feasible in pulsed high field magnets encouraged us to increase the investment into this endeavor and to start building a new generation of spectrometer and probes that are better adapted to these experiments. In addition, since most of the success of NMR is based on the very sensitive and abundant ^1H nucleus, the question raised by the NMR community was whether it will be possible to perform ^1H NMR at up to 60 Tesla (or 2.5 GHz). The answer to this question was not trivial: First, NMR spectrometers and probes had never been built for such high frequencies. Indeed, above 1 GHz there are considerable hardware changes necessary (the commonly used passively switched diodes for transmit/receive switches and classical schemes of passive protection from noise and receiver overload can not be used anymore). Second, the uncertainty in predicting a particular field value at high frequencies causes wide frequency jumps from shot to shot which require very high bandwidths that are much higher than those common for NMR spectrometers. Third, the resolution requirements for ^1H NMR are very high (the ^1H NMR chemical

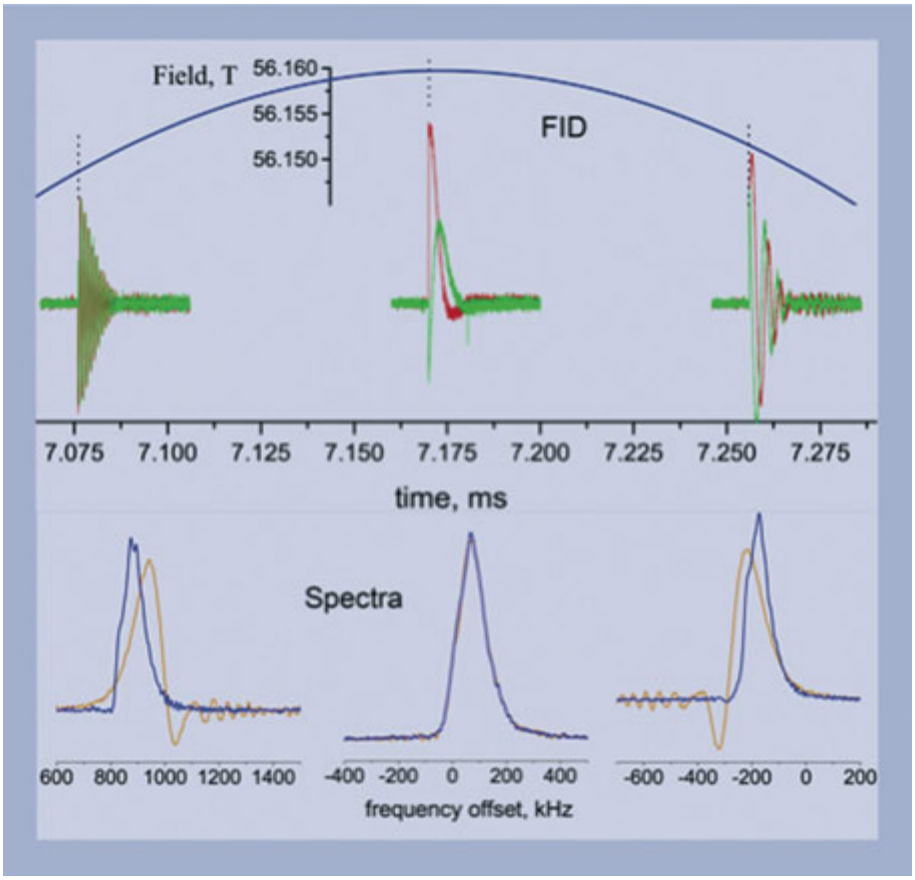

Fig. 2: Upper panel: Field vs. time segment (parabolic blue curve) near the field maximum. Three free induction decays (FIDs), real and imaginary signals, carrier subtracted. Each FID was excited by an RF pulse (carrier 2.4 GHz, duration 300 ns) at three different points in time with respect to the field maximum during three consecutive field pulses (the blue field curve belongs to the center FID, similar field curves were measured for the other two FIDs). Lower panel: Fourier transforms of the FIDs. Red: raw data; blue: spectra after demodulation with the actual field vs. time curve.

shift range is less than 15 ppm). Therefore, we decided to venture into an untouched frequency region for NMR, up to 2.5 GHz, and implement extreme time and frequency resolution (80 MHz real time bandwidth is in operation now).

Substantial progress was made recently[12,13]. In various steps we were able to increase the maximum frequency at which NMR has ever been observed to eventually 2.4 GHz. The spectrometer and the probe will be described elsewhere [14]. Fig. 2 shows a typical set of experiments performed with the new hardware.

These experiments show that NMR up to 2.4 GHz can be observed in pulsed high field magnets with sufficient sensitivity. The highest resolution achieved so far is about 12 ppm. While this is enough for most physics applications, it is not sufficient for broad applications with ^{1}H NMR. However, one has to stress that in these experiments the increase in resolution is solely based on a small sample size. The current results are in agreement with theoretical estimates of the coil's homogeneity. Thus, by redesigning the coils one can expect a substantial increase in the resolution that should make a large range of applications possible, also for ^{1}H NMR.

While the sensitivity is boosted by the pulsed high fields, NMR at lower, but static fields that allow for rapid signal averaging would outperform pulsed high fields. In particular, if the nuclear spin relaxation is not short enough or the magnetic pulses are not long enough one may have to employ prepolarization at lower fields. This would reduce the possible gain in sensitivity. With regard to resolution one has to say that static fields can be homogenized much more easily and that there is a wealth of methods available for increasing resolution in static fields that can probably not be used under pulsed conditions. Nevertheless, there are various systems (e.g., with strong electric quadru-

pole interactions) for which the resolution gain due to the higher fields will be superior. Therefore, we believe that NMR in pulsed high magnetic field will be most important for systems where the magnetic field drives physical effects. Here, new physics can be analyzed with a strong spectroscopic tool: NMR.

To conclude, our first steps towards NMR in pulsed high field magnets seem to prove that a new, promising research tool will be available soon.

[1] The author began this research, in collaboration with the IFW Dresden, in the beginning of the year 2002 when he was employed by the Max Planck Institute for the Chemical Physics of Solids. At the end of 2003, he took on a position at the IFW Dresden and continued his work there. In June 2005, he was appointed professor for experimental solid state physics at the University of Leipzig and he will continue these activities in Leipzig soon.

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