

Preface

The study of complex molecules requires high sensitivity and resolution for chemical analysis. This is why the NMR community pushes the development of ever more powerful superconducting magnets that generate stronger and more homogeneous magnetic fields every year. Today's NMR magnets are heavy giants installed in special NMR laboratories built to shield electromagnetic interference, control the temperature, and reduce magnetic field distortions in order to provide ideal experimental conditions in a small volume located inside the magnet. Besides the fact that samples must be taken to the magnet to be analyzed, they must fit in the limited space available in the magnet center. Large samples cannot be investigated in this way without cutting. This problem was already noted in the early days of NMR when the technique was identified as a potential tool to characterize rock formations in situ. Measuring properties of the pore structure as well as characterizing the saturating fluids downhole by NMR triggered the development of what today is called inside-out NMR. Here, instead of placing the sample inside the magnet, the apparatus is placed inside or at one side of the object.

The implementation of this concept requires the construction of sensors projecting considerable magnetic and radiofrequency (rf) fields outside the magnet and inside the sample under study. For more than 30 years well-logging tools used the earth's magnetic field as polarization field, but the low sensitivity and poor spatial selectivity limited their commercial success. Potential application of open NMR sensors to measure, for example, moisture in building materials or soil motivated engineers to use electromagnets to increase the magnetic field strength. However, these instruments were large, weighing up to 300 kg and operated at low frequencies like 3 MHz. Perhaps the most important step toward reducing the size of the magnets was the use of permanent magnets to generate the static magnetic field. This eliminated most of the power consumption of these NMR devices. During the late 1980s and early 1990s various magnet geometries have been proposed by different well-logging companies, and a number of research groups proposed small single-sided magnets generating magnetic fields of about 0.5 T external to the sensor. An example is the known U-shaped magnet geometry used by the NMR-MOUSE, which is obtained by opening the C-shaped geometry used in conventional closed magnets.

The big challenge faced when working outside the magnet is posed by the large inhomogeneities in both the magnetic and the radiofrequency fields. Under such experimental conditions even hard rf pulses act as selective pulses and off-resonance effects are considerable. Therefore, during the 1990s, several groups set their attention on understanding the response of the spin system to pulse sequences known from conventional NMR, like the Carr-Purcell-Meiboom-Gill (CPMG) sequence extensively used to measure the transverse relaxation time T_2 , when they are applied in the presence of a strongly inhomogeneous magnetic field. Chapter 2 provides the tools needed to evaluate the evolution of the magnetization to such pulse sequences implemented in the magnetic field generated by open NMR sensors. Besides providing the timing of some well-known pulse sequences and the phase cycle for the rf pulses required to eliminate unwanted signals generated by resonance offsets, typical features that must be considered at the time of implementing them are discussed. Moreover, a general expression is derived for the sensitivity of NMR experiments in inhomogeneous fields. The conclusions drawn from this analysis set the rules for optimizing magnet and rf coils to maximize the signal-to-noise ratio of single-sided sensors.

In the presence of inhomogeneous magnetic fields, relaxation times and diffusion coefficients are the key NMR parameters to assess sample composition and dynamics. To extract maximum information from relaxation and diffusion measurements, a number of numerical tools have been proposed. One of the most powerful ones is based on calculating the inverse Laplace transform of the signal decay to obtain the relaxation time distribution from a relaxation measurement. Although initially this transformation has been applied to 1D data sets, recently the possibility to extend it to 2D experiments in reasonable computation times has been reported. It opened the door to measure powerful multi-dimensional diffusion-relaxation and relaxation-relaxation correlation spectra useful to disentangle overlapping signals in a way similar to conventional multi-dimensional Fourier NMR spectroscopy. This methodology is described in detail in Chap. 3.

Although initially magnets were optimized to maximize sensitivity by maximizing magnetic field strength (at the expense of a strong static gradient) or the excited volume (at the expense of field strength), later, harder constraints have been imposed to the magnet design in order to generate convenient magnetic field profiles. Several of these magnets, including suitable rf coils, are presented in Chap. 4. A particularly useful field profile is the one that defines a uniform gradient along the depth direction. In the presence of such a field profile a slice parallel to the sensor surface can be excited at variable positions inside the object. Achieving depth resolution is useful to elucidate the depth structure of large samples. Moreover, furnishing these magnets with a set of coils that generate pulsed gradient fields along the two lateral directions, 3D spatial localization has been achieved. An important step toward a functioning open tomograph required the adaptation of single-point imaging sequences to work in inhomogeneous fields where multi-echo acquisition is mandatory to achieve maximum sensitivity. The different methods available to encode position during CPMG-like sequences are described in Chap. 5, where also

suitable pulsed field gradient sequences are discussed to measure molecular velocity in the presence of a strong background gradient.

Accepting the field inhomogeneities as unavoidable for open sensors, pulse sequences specially designed to minimize off-resonance effects have been proposed. A particularly challenging problem that attracted considerable attention over the years was the possibility to recover spectroscopic information from experiments performed in inhomogeneous fields. For a long time this was thought to be impossible because the static magnetic field inhomogeneities are usually orders of magnitude larger than those created by the microscopic structure of the molecules to be detected. In addition, terms in the spin Hamiltonian arising from chemical shifts or field inhomogeneities are formally identical. As a natural consequence, no radiofrequency pulse sequence was deemed capable of differentiating both types of interactions. A breakthrough was achieved in 2001 when an innovative alternative to recover a chemical-shift resolved spectrum in an inhomogeneous magnetic field was presented. The technique is based on matching the spatial dependence of the static and the rf magnetic fields, to generate nutation echoes whose phase is only sensitive to chemical-shift differences. This methodology and its implementation in a single-sided magnet are discussed in Chap. 6.

Although for decades magnetic field inhomogeneity was assumed to be a handicap inherent to these sensors, during the last years an important step ahead toward recovering spectroscopic resolution has been reported. In particular, it has recently been proven that highly homogeneous fields can be generated even outside a magnet by furnishing the main magnet with a shim unit built from small and adjustable permanent magnet blocks. Moreover, a way has been suggested to combine magnetic materials with different temperature coefficients to build a magnet with a temperature-compensated magnetic field. The strategy followed to homogenize the stray field of a single-sided magnet is discussed in Chap. 7.

Over the years, single-sided sensors have found applications in diverse fields such as the non-destructive testing of rubber and polymer products, food and life stock analysis, as well as the state assessment of objects of cultural heritage. Applications in the area of biological tissue are discussed in Chap. 8, while those in the area of material science and quality control are presented in Chap. 9. Finally, Chap. 10 intends to familiarize the reader with the particular hardware requirements of single-sided NMR.

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