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Waveguides for Micro-Magnetic Resonance

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1.1

Introduction

Nuclear magnetic resonance refers to the interaction of a system of nuclear spins exposed to a static magnetic field with an oscillatory field, usually in the radio frequency range (anywhere from 1 kHz to several GHz) [1]. In the overwhelming majority of cases, the changes in the spin state that result from this interaction are read out through a voltage induced by the spin precession into a surrounding conductor. Even though alternative readout approaches have been demonstrated, and have their advantages in certain cases, this type of inductive detection has proven to be both robust and easy to implement. Indeed, while the earliest demonstrations of nuclear magnetic resonance, pioneered by Rabi,[2] relied on the deflection atomic beams in inhomogeneous fields according to the spin state, NMR did not take off as a widely used tool until the invention of the direct induction method, independently discovered by Bloch[3] and by Purcell, Torrey, and Pound[4] in 1946.

Among other advantages, inductive detection allows the use of the same structure for both excitation and detection of the nuclear spin precession. Particularly in the context of the Fourier spectroscopy method,[5] this has become very useful. It is relatively easy to expose a sample to an oscillatory magnetic field by surrounding it with a suitable conductor, through which an alternating current is sent at the appropriate frequency. The precessing spins induce a measurable voltage in the same conductor. Of course, there are technical problems to be solved that arise due to the high power that is needed in some cases for excitation, while the induced voltages are very small and require exquisitely sensitive receivers. It is not uncommon for excitation RF power to approach several kW, whereas the power available for spin detection is typically of the order of only a few pW.

The earliest inductive NMR systems have almost exclusively relied on solenoid coils as excitation/ detection systems. As the applications of NMR have diversified, and new technologies have become available, other geometries have been explored. In particular, the advent of superconducting magnets with cylindrical bores has led to the development of saddle coils and related resonator geometries. Mag-

netic resonance imaging, in particular for medical applications, brought the need to accommodate much larger samples, which was met by the development of birdcage resonators. Hence, most of the current NMR detectors follow a roughly cylindrical form factor. There are some applications, though, which require a more planar geometry. In particular, the study of thin films, membranes, and interfaces is complicated in cylindrical detector systems. Special, flattened solenoid probes have been developed for the study of membrane proteins under solid-state NMR conditions [6]. As the magnetic fields, and, correspondingly, the Larmor frequencies used in MRI scanners have increased, uniform penetration of the radio frequency magnetic fields into the tissue has become more and more difficult. Since biological systems contain ionic solutions, non-conservative electric fields arising in the detector system need to be shielded from getting in contact with the tissue. The dielectric losses incurred from interaction between these electric fields and the tissue degrade the sensitivity of the detection, but they also lead to excessive power deposition in the tissue during excitation. As a solution, surface coils for localised MR imaging of human subjects based on circular or quadratically laid out strip lines have been proposed. [7] NMR spectroscopy is an extremely versatile tool. Nuclear spins turn out to be excellent spies. They are well insulated from the noisy electronic degrees of freedom to allow for long spin coherence life times, which is the basis of sharp spectral lines. At the same time, the nuclear Larmor frequency turns out to depend in subtle ways on the electronic environment. In combination, these two features make it possible to both accurately measure the nuclear Larmor frequency, and to interpret it in terms of the molecular environment that surrounds the nucleus.

Compared to many other spectroscopic techniques, NMR suffers from a major drawback: its relative insensitivity. While UV/VIS techniques, in particular fluorescence, can detect signals from single molecules with relative ease, NMR typically requires of the order of 10^{15} spins to resonate within a narrow bandwidth (1 Hz or so) in order for the signal to be measurable. To some extent, this can be alleviated by long measurement times. Since the signal/noise ratio only grows with the square root of the measurement time, sensitivity still limits the application of NMR in practice. The design of NMR detectors that offer optimal sensitivity has therefore been a long-standing research topic in magnetic resonance. Sensitivity is determined by the signal/noise ratio that can be obtained within a specified amount of time from a defined number of spins. Inductive detectors based on resistive metals invariably produce thermal noise. Under optimal conditions, where all non-intrinsic sources of noise have been eliminated by shielding, the blackbody radiation of the resonator structure itself leads to a noise voltage spectral density which is essentially independent of frequency, and scales proportionally to the square root of the ohmic resistance of the detector. The relationship between the NMR spin precession and the induced voltage signal has been discussed by Hoult and Richards in terms of the correspondence principle.[8] The induced signal strength from a single spin depends on the normalised magnetic field (generated by the detector per unit current) at the location of the spin. Hence, efficient detectors need to be designed such that the magnetic field they generate per unit current is maximal. This conflicts with the requirement of low resistance, which is important to keep the noise voltage small, and an optimal

compromise must be found in practice between the two. It has been well known for about two decades that the mass sensitivity (i.e., the signal/noise ratio per spin) of inductive detectors is roughly inversely proportional to the detector size. This can be rationalised by examining the normalised magnetic field and the radio frequency resistance of a particular detector geometry as a function of its overall dimensions. For example, the magnetic field generated by a single circular loop of diameter d made of a wire of thickness h is given approximately by $H/I = 1/(\pi d)$. If the geometry is scaled by a factor α , the H/I value therefore scales as α^{-1} . At typical NMR frequencies, the skin depth in Cu amounts only to a few μm . Therefore, as both the wire diameter and the loop diameter are scaled by the same factor α , the resistance of the structure remains roughly constant, as long as the wire diameter remains larger than the skin depth. As a result the signal to noise ratio is expected to scale roughly as $1/\alpha$. A similar argument can be made for solenoid coils. In practice, the observed scaling is weaker. Still, NMR detectors based on micro coils (i.e., with dimensions of tens to hundreds of μm) have been shown to provide very high mass sensitivities. This has formed the basis of hyphenated techniques, where upstream chromatographic separation is combined with downstream detection by an NMR system equipped with a micro detector.[9] Microfluidics is a rapidly expanding field of science and technology. The underlying idea is borrowed from micro electronics: to integrate complex functionality in a mostly two-dimensional layout, making use of efficient lithographic fabrication technologies. This lab-on-a-chip (LoC) approach has proven especially fruitful in enabling total analysis systems, which integrate sample preparation, chromatographic separation, and detection on single chip platform.[10] Since lithographic techniques allow the accurate reproduction of complex and very highly resolved features, microfluidic systems can be designed to mimic highly complex environments with great control and accuracy. This enables the culture of biological systems under artificial and highly controlled conditions, while closely mimicking the natural environment. This has become an invaluable tool for the study of differentiated cells, their development, and the interplay between different cell types. **REFS needed!!** NMR spectroscopy is uniquely suited to observe metabolic processes in live systems. It therefore has great potential as an observation tool in microfluidic culture assays. However, in spite of significant efforts, its use in the context of microfluidic devices is not yet widespread. There are a number of reasons for this. On the one hand, the planar geometry of microfluidic devices is not easily combined with common NMR detectors, which are typically designed for a cylindrical sample. Another limitation is the poor sensitivity of NMR, which is exacerbated by the small sample amounts typically available in microfluidic systems. As will become apparent in the following, micro stripline detectors are of particular interest in this context, since they inherently follow a planar geometry, and they can offer extremely high mass sensitivity. The first NMR probes based on a strip line geometry have been proposed in the context of magnetic resonance imaging. Their use for NMR spectroscopy at the microscope was first proposed by Maguire et al [11] in 2004. They integrated a stripline containing a small slot into a radio frequency resonator. The slot leads to current crowding, and consequently to a very large H/I value locally. This geometry provides excellent mass sensitivity, but the achieved

spectral resolution was still relatively poor. A few years later, van Bentum and Kentgens and coworkers proposed a stripline detector based on a symmetric geometry with ground planes on either side of the strip line. By tapering the transition in the width of the strip line broadening of the resonance lines due to magnetic susceptibility artefacts could be largely reduced, [12] leading to excellent performance in terms of resolution. While these probes were operated in a flow mode, with fixed capillaries acting as sample holders, this geometry has recently been modified by Finch et al. to a transmission line probe based on two identical planar conductors, which can accommodate an exchangeable microfluidic chip. Looking into the future, strip line based detector geometries offer significant potential for further advances in miniaturisation. Their fabrication using lithographic techniques is straightforward, in contrast to intrinsically three-dimensional geometries such as solenoids, and there is no reason why they could not be successfully applied to detectors an order of magnitude or more smaller than the ones that have been demonstrated so far. Another exciting possibility is the use of stripline detectors in travelling wave mode, rather than as resonators carrying standing waves. Travelling wave NMR, which been demonstrated in the context of magnetic resonance imaging and (macroscopic) NMR spectroscopy, could have significant advantages at the micro scale, since it allows the spatial separation of the sample and the detection circuitry. The remainder of this chapter is organised as follows: first, some theoretical aspects of strip lines and strip-line based resonators are examined in section 2. Section 3 provides a chronological overview of the development of micro-NMR strip line and micro strip based detectors, and finally, section 4 discusses some of the recently demonstrated applications.

1.2

Striplines and Microslots: Basics and Theory

1.2.1

Definition of a stripline

The presence of conducting bodies imposes boundary conditions on the free propagation of electromagnetic waves. For an ideal conductor (an idealisation that certain metals, including Cu and Ag, approach quite closely), the electric field vector must stay perpendicular to the surface, while the magnetic field vector is required to stay parallel. Wave guides are long metallic structures of (usually) constant cross section. Electromagnetic waves of different types (modes) can propagate in the longitudinal direction in such structures. They are classified as transverse electric (TE) or transverse magnetic (TM) waves. In TE waves, the electric field has no component in the longitudinal direction, while the longitudinal magnetic field vanishes for TM waves. Both TE and TM wave modes can only propagate if the wave length is smaller than the lateral dimensions of the wave guide. This leads to a minimum frequency (often referred to as the cutoff frequency) for propagating modes. Also, the relationship between the wavelength and the frequency for TE and TM modes is non-linear, leading to dispersion. An additional type of propagating mode becomes possible if the walls

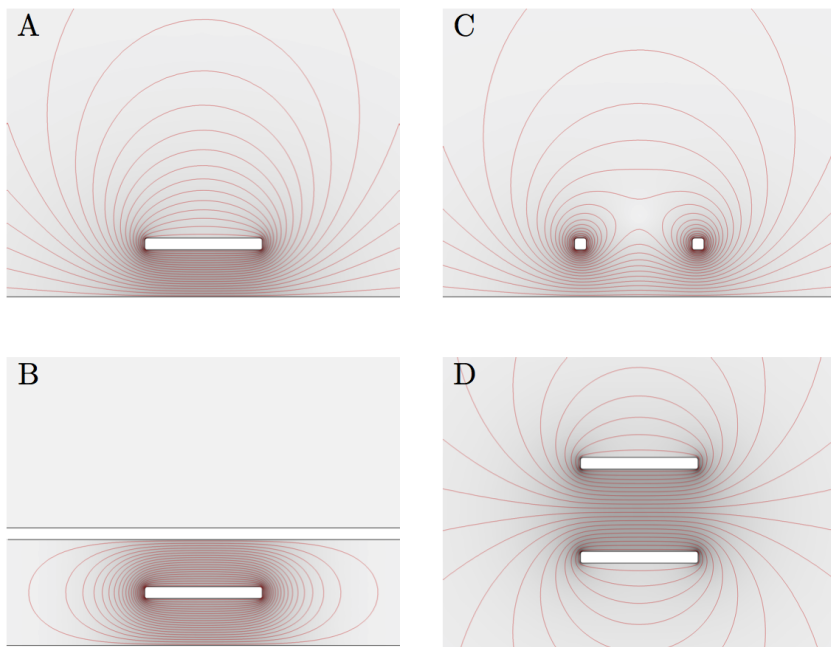


Figure 1.1 Cross section of some typical planar transmission line geometries, including magnetic field lines of the TEM mode. A: microstrip, B: stripline, C: microslot, D: parallel plate transmission line

of the wave guide are divided into several (at least 2) mutually insulated sections. In this case, an oscillatory voltage can be sustained between the separate conductors. Under these conditions, a propagating modes exist *both* the electric and magnetic fields are transverse. Such TEM modes do not exhibit a cutoff frequency, and in general exhibit a linear relationship between wavelength and frequency. Frequencies of interest in magnetic resonance lie below 1.5 GHz. With usual dielectrics, this yields wave lengths of 20 cm or more. Therefore, TEM modes are commonly used in order to transport NMR signals, often in coaxial cables. This is different in electron paramagnetic resonance (EPR), where frequencies up to several hundred GHz occur. This requires the use of rectangular wave guides, in some cases with corrugated metal interior surfaces. Fig. 1.1 shows some examples of common wave guide cross sections. Among these, the most familiar to NMR spectroscopists is that of the coaxial cable. Planar wave guide structures such as the microstrip (Fig XXXX b) and the stripline (Fig XXX c) are conveniently implemented on printed circuit boards, [13] and are very commonly used in the design of radio frequency and microwave circuits.

1.2.2

Characteristic Impedance and Transport Characteristics

For TEM modes, it is possible to attribute a current and a voltage amplitude to the travelling wave by integrating along the electric / magnetic field lines in the cross section. While the absolute voltage and current amplitudes depend on the level of wave excitation, their ratio (measured in Ohm) is a constant given purely by the cross section geometry, and the dielectric and magnetic properties of the insulating medium. This ratio is known as the characteristic impedance Z_0 of the wave guide. Coaxial cables are commonly designed for a characteristic impedance of 50 Ohm.

1.2.3

Theory of TEM Wave Modes

Maxwell's curl equations couple the magnetic field \mathbf{H} and the electric field \mathbf{E} . If we assume a harmonic time evolution of the fields with angular frequency ω , they become

$$\nabla \times \mathbf{H} = j\omega\epsilon\mathbf{E} \quad (1.1)$$

$$\nabla \times \mathbf{E} = -j\omega\mu\mathbf{H} \quad (1.2)$$

where $j = \sqrt{-1}$ is the imaginary unit, and ϵ and μ represent the electric permittivity and magnetic permeability of the insulating medium, respectively. In order to analyse a TEM mode, we assume the axis of the transmission line to be aligned with the z direction. The two curl equations can be combined to the Helmholtz equation

$$(\nabla^2 + k^2)\mathbf{E} = 0, \quad (1.3)$$

where $k = \omega\sqrt{\mu\epsilon}$ is the wave number. If we assume a harmonic dependence in the z direction of the two transverse components, proportional to e^{-jkz} , it is easily shown that the transverse components must satisfy Laplace's equation, i.e.,

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) E_{x,y} = 0. \quad (1.4)$$

A similar argument leads to the same result for the transverse magnetic field. The electric and magnetic field distribution in the cross section of a transmission line are therefore solutions to Laplace's equation. The fields satisfy the boundary conditions $\mathbf{E} \cdot \mathbf{n} = 0$ and $\mathbf{H} \times \mathbf{n} = 0$, where \mathbf{n} is the surface normal. It is useful to note that the field distributions follow the same laws as in the case of completely static fields. In particular, this means that the field distribution inside a transmission line is *independent of the frequency*. Transmission lines are therefore inherently broadband devices, with no lower limit to the frequencies they can carry. In theory, there is no upper limit for the propagation of the TEM mode either; however, the excitation of TE and TM modes complicates the situation at very high frequencies. For this reason, coaxial transmission lines are only used up to frequencies of several tens of GHz. In addition, dielectric losses in commonly used insulators become intolerable at very high frequencies.

1.2.4

Modelling of TEM modes

Since the transverse electric and magnetic field distributions for TEM modes are solutions of the two-dimensional Laplace equation, they are easily computed for any geometry using a finite element or finite difference approach. It should be noted that the electric field is curl-free. Therefore, it can be represented as the gradient of an electrostatic potential $\phi(x, y)$, which also satisfies the Laplace equation. Computing the transverse field distribution therefore reduces to a simple Dirichlet problem, where fixed potential values must be attributed to the conductor surfaces:

$$\nabla^2 \phi(x, y) = 0 \quad \text{on } B, \quad \phi = V_{1,2,\dots} \quad \text{on } \partial B_{1,2,\dots}, \quad (1.5)$$

where B denotes the dielectric cross section, and $\partial B_{1,2,\dots}$ represent the conductor surfaces, and $V_{1,2,\dots}$ are the electrical surface potentials. The electric field of a propagating TEM mode is then given by

$$\mathbf{E} = e^{-\gamma z} \left(-\frac{\partial \phi}{\partial x}, -\frac{\partial \phi}{\partial y}, 0 \right), \quad (1.6)$$

where $\gamma = \alpha + jk$ is the propagation constant, which describes both the oscillatory propagation of the wave in the z direction with wave number k and its gradual attenuation with decay constant α .¹⁾

The magnetic field distribution is easily found using the the curl equations:

$$\mathbf{H} = e^{-\gamma z} \left(\frac{1}{\eta} - \frac{j\alpha}{\omega\mu} \right) \left(\frac{\partial \phi}{\partial x}, -\frac{\partial \phi}{\partial y}, 0 \right), \quad (1.7)$$

where the characteristic impedance of the medium η is given by

$$\eta = \sqrt{\frac{\mu}{\epsilon}}. \quad (1.8)$$

Note that in the case of $\alpha = 0$, the magnetic and the electric field are *in phase*, whereas a positive attenuation constant $\alpha > 0$ leads to the magnetic field phase lagging behind the electric field. The time-averaged power transported by the TEM wave is given by real part the Poynting vector as

$$\Re(\mathbf{S}) = \frac{1}{2} \Re(\mathbf{E} \times \mathbf{H}^*) = p_t \hat{\mathbf{z}}, \quad (1.9)$$

where the cross-sectional density of power $p_t(x, y)$ is

$$p_t(x, y) = \frac{e^{-2\alpha z}}{2\eta} \left[\left(\frac{\partial \phi}{\partial x} \right)^2 + \left(\frac{\partial \phi}{\partial y} \right)^2 \right]. \quad (1.10)$$

1) It should be noted that the foregoing treatment is only strictly exact in the limit $\alpha \ll k$. However, for transmission lines composed of polymer dielectrics and good conductors, this is almost always true to a good approximation.

The relative power loss per unit length is therefore given by

$$\frac{1}{p_t} \frac{\partial p_t}{\partial z} = -2\alpha. \quad (1.11)$$

At every cross section of the transmission line, it is possible to compute the electrical potential difference between the two conductors by a path integral between the conductor surfaces

$$V(z) = \oint_1^2 \mathbf{E}(x, y, z) \cdot d\mathbf{s}, \quad (1.12)$$

Similarly, the current flowing in the conductor can be obtained using Ampere's law

$$I(z) = \oint \mathbf{H}(x, y, z) \cdot d\mathbf{s}, \quad (1.13)$$

where the integration path in this case is a closed loop around the conductor.

It is easily shown that the voltage and current thus obtained satisfy the equations

$$\frac{d^2 V}{dz^2} = \gamma^2 V(z) \quad (1.14)$$

$$\frac{d^2 I}{dz^2} = \gamma^2 I(z). \quad (1.15)$$

These equations are useful to describe the behaviour of transmission lines when integrated into electrical circuit networks. In general, they can be solved by a superposition of two waves travelling in opposite directions:

$$V(z) = V_0^+ e^{-\gamma z} + V_0^- e^{\gamma z} \quad (1.16)$$

$$I(z) = I_0^+ e^{-\gamma z} + I_0^- e^{\gamma z}. \quad (1.17)$$

The ratio

$$Z_0 = \frac{V_0^+}{I_0^+} = \frac{V_0^-}{I_0^-} \quad (1.18)$$

is known as the characteristic impedance of the transmission line. Its value depends entirely on the geometry of the transmission line cross section and on the dielectric and magnetic properties of the insulator.

1.2.4.1 Losses in Transmission Lines

There are two main contributions to the power losses in a transmission line. On the one hand, there are dielectric losses due to the repeated polarisation and depolarisation of the insulating medium. These are proportional to the magnitude of the electric fields. The dielectric properties of most insulator materials are only very weakly frequency dependent; the dissipated power therefore tends to be proportional to the frequency. The dielectric dissipation of a material can be expressed by an imaginary component in its dielectric permittivity $\epsilon = \epsilon' + i\epsilon''$. Often, the loss tangent, defined as $\tan \delta = \epsilon''/\epsilon'$ is used in order to characterise the material. A second

(and, in the present context, often dominant) source of losses is the finite conductivity of the metallic surfaces. A plane electromagnetic wave impinging on an imperfect conductor penetrates into it only to a finite depth δ_s , known as the skin depth. This is because the tangential component of the magnetic field at the boundary induces in the surface a current which cancels the magnetic field deeper inside metal. Since this current is sustained against a finite ohmic resistance, it leads to heating and therefore to a loss of power from the electromagnetic wave. The dissipated power depends linearly on the magnetic field at the surface of the conductor. If the dimensions of the transmission line cross section are much larger than the skin depth, it is possible to express the average dissipated power per unit surface area as

$$P_\delta = \frac{1}{2} |H_\parallel|^2 R_s, \quad (1.19)$$

where R_s is the surface resistance of the metal. It depends on the material's conductance and the skin depth as

$$R_s = \frac{1}{\sigma \delta_s} = \sqrt{\frac{\omega \mu}{2\sigma}}, \quad (1.20)$$

where δ_s is the skin depth, and σ represents the conductivity. For pure Cu, $\sigma = 5.9 \cdot 10^7 \text{ S/m}$, which translates into a surface resistance of about 10 m Ω at 100 MHz, and about 35 m Ω at 1 GHz. The losses lead to a gradual attenuation of a travelling TEM mode, as reflected in the real part of the propagation constant γ . The conductive and dielectric losses are additive, such that we can write

$$\alpha = \alpha_d + \alpha_c. \quad (1.21)$$

In the following, we examine some planar transmission line geometries, and the relationship between their geometry, characteristic impedance, and attenuation constants.

1.2.5

Magnetic Fields and Losses in Transmission Lines, Striplines, Microstrips and Microslots

The magnetic and electric field distributions of the TEM mode in some planar transmission line geometries are shown in Fig XXX. Fig XXa shows a stripline, symmetrically bounded between two ground planes. The magnetic field lines encircle the central conductor, producing two areas of very high field homogeneity which can be used as sample locations for NMR spectroscopy. The stripline, shown in Fig. XXb, exhibits a similar field geometry. However, since there is only a single ground plane, the magnetic and electric fields penetrate into the free space above. This is less pronounced in practice than in the idealised computation shown here, since the dielectric constant of the insulator means that the electric field remains partially captured inside it. Nonetheless, the open geometry can lead to radiation losses, which must be kept to a minimum by external shielding. Fig. XXXc shows a microslot line. In

this case, there are two independent conductors, which can in principle carry different electrical potentials. This geometry is therefore capable of supporting more than one TEM mode. However, in the present context, only the common mode shown in Fig. XXXc is of interest. Compared to the similar microstrip geometry, the magnetic field is concentrated in the space immediate above the pair of conductors.

1.2.5.1 Transmission Line Resonators

- Dimensions and eigenfrequencies
- Q factor and sensitivity
-

1.2.6

Waveguides in Micro-NMR Literature

1.2.6.1 Microstrip NMR Probes in MRI

Microstrips were introduced into magnetic resonance imaging long before their benefits for micro-scale NMR spectroscopy were realised. For example, Bridges proposed a resonator based on a cylindrical arrangement of microstrips inside a common ground cylinder [14]. This can be seen as a short piece of multi-conductor transmission line, capable of supporting many different TEM modes. As Bridges showed, one of these is characterised by a highly homogeneous B1 field on the inside. A similar design has been described later by Bogdanov and Ludwig [15]. The arrangement and its eigenmode is similar to the birdcage coil [16], which has become the mainstay of volume detectors in MRI. As the magnetic fields available for MRI increased, it became more important to limit the exposure of the human subject to radio frequency electric fields. RF heating of the sample, and, concomitantly induced noise, become more difficult to manage at higher magnetic fields. With the advent of 3.5T and later 7T NMR scanners, strategies for limiting the penetration of electric fields into the sample, as well as for reducing radiation losses, were needed. Zhang et al [7, 17] demonstrated that single square loop surface coils made from a microstrip provided significant advantages over conventional loop coils of comparable dimensions. These loops consist of a microstrip designed to support a $\lambda/4$ standing wave, with either an open or a shorted end. At higher fields, the quarter wavelength requirement limits the size of the coils that can be built on this basis. However, planar multi-loop coils supporting higher-order modes ($3\lambda/4$ and higher) have also been demonstrated [18]. Zhang et al. developed an elegant version of the stripline volume detector, in which the coupling between the lines is accomplished by simply dividing the back-plane conductor into two halves in the axial direction of the cylinder. This avoids the need to connect each strip separately through a matching network [19]. Standing wave microstrip resonators have been used for micro-imaging of the rat spinal cord at 4.7T with a resolution of 0.15mm, and to build anatomical head coils for human subjects [20]. Vaughan et al. built an actively de-tuneable version of a transmission-line head coil, in which the individual microstrips can be shunted to the ground plane by means of DC-biased PIN diodes [21]. This allows the simultaneous use of localised receiver coils inside the volume resonator without mutual coupling artefacts.

Lee et al. proposed an array of planar microstrips [22, 23] for phased-array detection [24, 25]. Their design exploits an intriguing property of identical parallel and coplanar microstrips: standing wave modes in adjacent strips are automatically decoupled from each other by symmetry. Phased microstrip array detectors have since been used successfully as external coils for prostate imaging [26], and an array of mutually decoupled microstrip loops has been used by Adriany et al for parallel acquisition and individual control of RF phases and amplitudes in a human head coil at 7T [27]. It should be noted that in cylindrical and other non-planar arrangements, identical parallel microstrips are no longer automatically decoupled. Decoupling can be achieved either capacitively, or inductively [28]; the latter approach has the advantage that the coupling and decoupling mechanisms follow the same frequency dependence, i.e., the decoupling is broad-band. The properties of microstrip resonators and other MRI detector geometries have been compared in numerical and in some cases experimental studies by several authors [29–31]. Wang and Shen [29] compared the sensitivity, power deposition, and field distributions for birdcage, microstrip, and TEM coils at 7T by finite element computations. They found microstrip coils to provide superior SNR while depositing less power into the tissue than birdcage or TEM resonators. Ipek et al. [31] experimentally compared a radiative dipole antenna with a microstrip resonator of similar dimensions for prostate imaging at 7T. The radiative antenna design is optimised to produce a Poynting vector perpendicular to the plane of the antenna, in order to radiate into the tissue and reach deeper lying structures. By contrast, the microstrip resonator does not radiate efficiently, the main direction of its Poynting vector is in the axial direction (and its time average vanishes due to the standing wave resonance). Ipek et al. found this to be reflected in deeper reaching B1 fields for the antenna. However, the power deposited in the tissue was lower, and the SNR for areas closer to the receiver was higher for the microstrip resonator. ###

Microfluidic NMR It was demonstrated in the early 1990s that micro-solenoid coils, with diameters more than an order of magnitude smaller than conventional detectors, exhibit very high mass sensitivity [32–34], and thus allow direct combination of chromatographic separation techniques such as capillary electrophoresis [35–37] and high-pressure liquid chromatography [38]. Solenoidal micro coils have also been used successfully for micro-imaging [39, 40], achieving resolutions approaching the single cell length scale. In solid-state NMR, micro coils have been used for statically, for example for studying spider silk [41], but also under Magic-angle spinning (MAS) NMR has been made possible by attaching the micro-scale sample to a conventional MAS rotor, and surrounding it by a micro-solenoid [42]. Another possibility is to insert a tuned micro coil into the MAS rotor, and spinning it together with the sample. The coil is then inductively coupled to the macroscopic probe coil [43, 44]. In recent years, MAS probes capable of very high spinning speeds, exceeding 100kHz, have been demonstrated, and are now commercially available. In these systems, the sample diameter has to be kept small in order to limit the inertial forces. This has inevitably led to smaller and smaller samples, and the dimensions of the rotors and coils of the most recent designs approach those of the micro-solenoids that were introduced for liquid-state NMR in the 1990s [45]. Solenoid micro coils have also been used for remote detection in the context of microfluidic devices. In this elegant ap-

proach, position, velocity, and in some cases, chemical information is encoded into the spin phase and polarisation inside microfluidic system, by way of a macroscopic coil which surrounds it. The fluid then flows out of the microfluidic device, and is led in a capillary through a micro coil, where the NMR signal is recorded. In this way, the velocity distribution as well as chemical reaction dynamics in microfluidic systems have been characterised in real time [46–54].

1.2.6.2 NMR and Microfluidics: Planar Detectors

With the success of miniaturised solenoid coils, it became conceivable to integrate NMR spectroscopy with emerging microfluidic lab-on-a chip technology. Typical sample volumes in microfluidics, ranging from a few μL down into the pL range, are comparable to the volumes of some of the micro-solenoids that had proven superior mass sensitivity performance in hyphenated chromatography-NMR integrations. However, Lab-on-a-chip devices are typically planar, fabricated through lithographic processes, and the liquid volumes they contain are separated from each other by relatively large distances. Integrating solenoid coils into such structures, while not impossible, presents significant fabrication challenges [55]. As a possible solution, planar spiral coils were explored extensively. The first demonstration, by Stocker et al. [56], placed a sample droplet directly in contact with the micro coil. Trumbull et al. integrated a single loop inductor with a microchip-electrophoresis system [57]. The metal structure for the loop inductor was fabricated through a lift-off process. This provides very tight structural control, but the metal thickness that can be deposited is limited to about $1\ \mu\text{m}$. Since this is less than the skin depth, it probably limited the sensitivity of the system. Two different chip substrates were used. In one case, the fluidic structures were fabricated using a polyimide photoresist, while in the second one, they were etched into pyrex glass. The polyimide structure provided considerably better spectral resolution, probably due to the closer match in susceptibility between the polyimide and water. While NMR spectra of test samples were successfully collected, the sensitivity of the device was not found to be sufficient for a credible integration with capillary electrophoresis. Later implementations involved fabrication of the spiral coil structure by lift-off lithography and subsequent electroplating onto a glass microfluidic chip [58]. This allows thicker conductors, significantly reducing ohmic losses. Microfluidic probes based on this design [59] reached limits of detection of $260\ \text{nMol}\ \sqrt{\text{s}}$ at $470\ \text{nL}$ probe volume, and $20\ \text{nMol}\ \sqrt{\text{s}}$ at $30\ \text{nL}$ probe volume (LoD values scaled to $600\ \text{MHz}$ proton frequency). However, the spectral resolution was quite poor, insufficient to resolve homonuclear J couplings in the ^1H spectra. While the sample was held in a circular chamber underneath the spiral coil in Massin et al.'s design, better resolution was achieved by arranging it in a linear channel aligned with the magnetic field [60], making it possible to monitor the on-chip condensation of benzaldehyde and aniline [61]; further applications of planar spiral coil designs to microfluidic reaction monitoring followed [62, 63]. Planar spiral coils have also been applied to EPR spectroscopy [64] at the micro scale.

Placing planar coils on both sides of the sample leads to the concept of micro-Helmholtz coils. These provide potentially high sensitivity and B1 homogeneity, but

present considerable fabrication challenges. An elegant implementation has recently been described by Spengler et al. [65, 66]. Phased arrays provide another potential approach to planar micro-NMR detectors. A proof of concept has been given by Gruschke et al, who have demonstrated a system of 7 partially overlapping coils fabricated using a wire-bonding process [67]. This detector has been used successfully to image human skin samples [68] and to study porous media using a single-sided, permanent magnet spectrometer [69].

Microstrips for Micro-NMR

Given the difficulty of integrating three-dimensional coils with planar microfluidic devices, and the benefits that linear structures aligned with the B_0 magnetic field offer in terms of field homogeneity, it is not surprising that microstrip detectors were considered for integrating microfluidics and NMR. A problem that arises immediately is that transmission line resonators require longitudinal dimensions that are of the order of the wavelength, which amounts to tens of centimetres for typical NMR Larmor frequencies. Maguire et al. therefore proposed slotted microstrips as a means to concentrate the RF magnetic field, and therefore the sensitivity, to a mm-sized area [11, 70]. Their design was based on a single microstrip conductor of 0.3 mm width and about 5 mm length, fabricated using RF printed circuit board material using standard wet-etching techniques. At the centre of this structure, a square-shaped piece of the Cu conductor was removed from the microstrip. This concentrates the current into the narrow remaining conductor bridges, leading to a corresponding increase in local magnetic field. This yielded a mass sensitivity significantly better than what had previously been achieved with spiral planar coils. At the same time, a half-height line width of about 1.1 Hz was obtained, significantly superior to any other planar micro-NMR detector described up to that point. However, the baseline resolution was still relatively poor (>50 Hz at 0.5%). Nonetheless, one- and two-dimensional ^1H NMR spectra of sucrose and of ribonuclease A were obtained successfully. Microslot probes of this type have since been applied successfully for studying the metabolism of biological systems. In one of the first credible demonstrations of microfluidic NMR metabolomics, a microslot detector was applied to obtain NMR spectra of a metabolite concentrate from a cell line by Krojansi et al [71]. More recently, the exa-metabolome of a tumour spheroid was observed directly by combining the microslot detector with an evaporation-driven perfusion micro-device [72].

Non-Resonant Detectors

The microstrip geometry has also been used to build non-resonant NMR saddle coils [73]. In this approach, a saddle coil is defined by microstrips fabricated on a flexible printed circuit board, which is then wrapped in a cylinder to serve as a saddle-coil NMR probe. The microstrips are designed to have a specific impedance of 50 Ohm, and are terminated by a 50 Ohm resistor between the microstrip and ground conductors. Unlike typical NMR detectors, this system does not rely on an electromagnetic resonance (standing wave) in order to couple the detector to the transmitter/receiver

system [74]. Instead, a travelling TEM wave is directly coupled to the precessing nuclear spins. The most notable advantage of this approach, commonly referred to as travelling-wave NMR, is its broad-band nature, which makes it simple to perform multinuclear NMR experiments. The saddle coil system mentioned above has been used, without re-tuning, to obtain ^1H , ^{13}C , ^{19}F , and ^{31}P spectra at 0.52 T. Broad-band switching between transmission and receiver mode has been realised mechanically by way of a Reed relay. Linear non resonant microstrip detectors have been investigated by Zhang et al [75], who have also performed a direct comparison of the sensitivity of a microstrip operated in non-resonant and in standing-wave mode. In a non-resonant system, the spin precession is coupled into the TEM mode of the transmission line in both directions. Therefore, Zhang et al used transmit/receive switches at either end of the transmission line, and combined the signal power from both before pre-amplification [76]. Interestingly, the SNR from this setup was found to be the same as in the traditional standing-wave operation. Travelling wave excitation and detection has been considered as a way to circumvent limitations of high-field full body MRI, where the dimensions of the sample are comparable to the wavelength of the RF radiation. In conventional near-field detectors, this leads to uneven phase and amplitude of the RF signals throughout the sample. Brunner et al. have demonstrated that MR images with high sensitivity and good homogeneity can be obtained at 7T by travelling wave detection [77]. In this case, the conductive bore casing acts as a cylindrical transmission line, and the TE₀₁ mode is excited using circularly polarised patch antenna near the entrance to the bore. The possibility to place the detector and excitation structures remotely from the sample is another advantage of travelling wave systems over conventional standing wave MR detectors. Travelling wave detection has also been investigated directly in a coaxial cable running vertically through the bore of a NMR magnet, with the sample taking the place of the dielectric in the homogeneous area of the magnet [78], and a similar design using a planar transmission line has been proposed, but not yet demonstrated experimentally. A related concept has been proposed recently by Fratila et al, who directly connected a planar micro coil between the coaxial transmission line and a matched ohmic termination [79].

Stripline Detectors

Striplines and microstrips are closely related, the main difference being that the magnetic and electric fields in a stripline are bounded on both sides by ground planes, in contrast to the one-sided microstrip. Striplines have been introduced to microwave technology earlier than microstrips, but are less commonly used in contemporary microwave circuits due to more complex fabrication. However, they do offer some advantages when used as NMR detectors. Kentgens et al. have built a stripline detector for micro-NMR on printed circuit board, with the sample replacing the dielectric on one side of the stripline [80]. A constriction in the stripline at the location of the sample causes a concentration of the current, and correspondingly, the RF magnetic field. A PCB material with a low loss tangent was used to optimise sensitivity. The stripline was tuned and matched to both the ^1H and ^{13}C larger frequencies by in-

serting it as a short to ground at the end of transmission line resonators made from semirigid coaxial cable. This arrangement allows ^1H - ^{13}C double resonance experiments; however, no such results were reported [80]. The sample volume was about 100 nL, and a mass sensitivity of 10^{13} spins/Sqrt(Hz), or about 0.1 nMol sqrt(s) was obtained. It should be noted, however, that this refers to the single-scan detection limit, and that a more realistic measure of sensitivity would take into account the delay required for the acquisition of multiple transients. The B1 homogeneity of the detector was quite good, at a 810/90 ratio of about 60%. However, the B0 homogeneity was relatively poor in this initial design. A more sophisticated variant of this design was present by Bart et al [81]. The improved stripline has been designed directly as a symmetric RF resonator, supporting a $1/2$ lambda standing wave with current nodes at the ends. A constriction in the width of the stripline at the centre causes a local increase in magnetic field, and a concomitant increase in local sensitivity. The resonator is arranged vertically, parallel to the static magnetic field, minimising susceptibility broadening artefacts. The geometry of the resonator, including the constriction width, length, and angle of the taper, had been carefully optimised using finite element computations [12] for sensitivity and B0 and B1 homogeneity. Bart et al. showed that the length/width ratio of the constriction is crucial for sensitivity, and found that ratios between 5 and 10 are optimal. Steep tapers were found to be preferable in terms of sensitivity, but produce greater B0 homogeneity artefacts. The probe was fabricated by Cu vapour deposition and subsequent electroplating onto a Si substrate, which served as a dielectric for the stripline. On one side, the sample channel is etched into the Si, replacing a part of the dielectric. Ultra pure, low-conductivity Si is an excellent insulator at room temperature, and exhibits a low loss tangent. However, it typically carries surface layer rich in defects, which lead to high dielectric and ohmic losses. To avoid these, Bart et al. deposited a layer of amorphous silicon (a-Si) before the metallisation. While this substantially increased the quality of the resonator, the achieved sensitivity was still about an order of magnitude less than theoretically predicted. Nonetheless, the stripline probe produced the highest quality microfluidic NMR spectra at the time. A limit of detection of $\text{nLODw}=22.2$ nMol sqrt(s) was demonstrated for the anomeric proton in sucrose in a sample volume of 600 nL, at a spectral resolution of better than 1 Hz. Bart et al. also showed that a useful metabolomic spectrum could be obtained from a sample of human cerebrospinal fluid, even though this required several hours of acquisition time. This type of stripline probe has meanwhile been adapted to a number of interesting applications. The flow-through probe described by Bart et al has been used for inline reaction monitoring [82]. A stripline resonator similar to the first one described by van Bentum et al [83] has recently been used to obtain ^{75}As NMR spectra from single crystalline epitaxially grown films of $\text{Al}_x\text{Ga}_{(1-x)}\text{As}$, in which 5 separate As sites could be distinguished [84]. A stripline probe has also been integrated with a electrochemical conversion assay. In order to accumulate a sufficient concentration of the electrochemical reaction products, the EC system was integrated with a solid-phase extraction column, the elute from which was then fed into the flow-through stripline NMR probe [85, 86]. An interesting recent development is the hyphenation of supercritical CO_2 chromatography with NMR detection. SCF chromatography

exploits the relatively low viscosity of SCF solvents, which reduce the back pressure at high flow rates compared to HPLC systems. This allows higher throughput than standard HPLC, as well as the separation of molecules that are not soluble in typical HPLC solvents. The combination of SCFC with NMR detection would be a natural fit, since the solvent does not produce an NMR signal. Also, the higher throughput means that potentially larger amounts of sample can be used and collected, which facilitates NMR observation. Finally, SCF CO₂ is a very low viscosity solvent, which can have a positive impact on spectral resolution, particularly for small molecules. However, the direct in-line hyphenation of SCFC with NMR detection has not yet been reported. A proof of principle has been given by Tayler et al [87], who used an HPLC storage loop to collect fractions from SCFC, which were then dissolved in methanol and injected into a stripline flow probe. Stripline and microstrip probes offer control over the detailed amplitude and phase distribution of the RF magnetic field. This opens up many possibilities to integrate spatial information into the NMR signal collection, which have only sparsely been explored to date. Tijssen et al. showed that a tapered strip line produces a well-defined B1 gradient, and have used this in order to simultaneously acquire NMR spectra of plugs of different composition injected one after the other into the sample capillary [88]. The same system can be used for continuous-flow reaction monitoring. Tijssen et al also demonstrated that the B1 gradient generated by the tapered stripline can be used to compensate for B0 inhomogeneities, by acquiring a spatially encoded signal from which the high-resolution NMR spectrum can be retrieved by data processing. This possibility may have important applications in permanent magnet NMR systems. Finally, it should be noted that the stripline design is not only of interest in NMR spectroscopy, but also in electron paramagnetic resonance. Yap et al. have recently described a pulsed Ku-band (17 GHz) EPR system based on a micro-stripling resonator. In their design, several variants of the tapered stripline resonator were explored, including one where the sensitive area is formed by a narrow, U-shaped turn in the stripline conductor. Using this resonator, very high sensitivity and Rabi (nutation) frequencies in excess of 210 MHz have been obtained. Klotz et al. have used a co-planar stripline pair to manipulate single electron spins trapped in quantum dots [89]. This type of magnetometer, as well as related systems based on NV-centre defects in diamond REF needed, could become important as highly sensitive NMR detectors in the future. Waveguide structures have also been used extensively in the design of probes for dynamic nuclear polarisation, which require simultaneous irradiation at NMR and EPR frequencies (see below).

1.2.6.3 Parallel Plate Transmission Lines

Parallel plate transmission lines (PTL), comprised of two parallel conductors of equal width, share some of the characteristics of both stripline and microstrip waveguides. In particular for large w/h ratios, the electric field is largely contained in the dielectric space between the conductors. However, there is some spillover into the surrounding space, and the magnetic field lines are not contained, but loop around each conductor, as shown in Fig. XXX. Like microstrips, and in contrast to striplines, PTL do not support a pure TEM mode in general, due to the difference in dielectric constant

between the dielectric material and the surrounding air. In the context of magnetic resonance detectors, the PTL geometry is a natural fit with planar samples, and it is somewhat surprising that it has not been exploited more extensively to date. Jasisnski et al have built a micro imaging NMR probe head using a resonator based on a PTL of 5 mm length and 0.3 mm width [90]. The w/h ratio had been optimised using two-dimensional finite element calculations; it was found that w/h values in the vicinity of unity provided a good compromise between RF homogeneity, filling factor, and sensitivity. The PTL was tuned and matched to a 50 Ohm coaxial cable, giving an unloaded Q factor of 120, in good agreement with the finite element simulations. The resonator was placed in a magnetic field of 11.7T, with the magnetic field direction normal to the conductor planes. High quality images of $24 \times 24 \times 300$ μm resolution on 128×128 points could be obtained with this detector in about 45 minutes. A similar detector was built by Finch et al [91]. Their geometry was an adaptation of the stripline probe proposed by Bart et al. [81], consisting of a half-wave resonator with the waveguide axis parallel to the magnetic field, and a constriction at the location of the sample. Unlike earlier “microfluidic” NMR probes, which used fixed capillaries requiring fluidic sample connections, the probe by Finch et al was designed to accommodate a wide range of microfluidic devices manufactured from PMMA sheet material by either by hot embossing, or by inexpensive rapid prototyping techniques based on a digital laser cutting system. Starting from a requirement of a sample chamber volume of 2 μl , Finch et al. used a numerical search algorithm in combination with a 3D finite element model of the resonator to optimise simultaneously the probe chamber dimensions (width \times length), and the corresponding dimensions of the constriction in the resonator. The optimisation was balanced between the conflicting targets of high sensitivity and RF homogeneity, resulting in a compromise design. This probe achieved a frequency-domain limit of detection of $\text{nLOD}_w = 2 \text{ nMol} \sqrt{\text{s}}$ (based on signal averaging over multiple transients), at a line width of 1.78 Hz (at 7 T). Importantly, the line widths at 0.5% and 0.1% height were inside of a Lorentzian line with the same half-width. This baseline resolution is of particular importance in metabolomic studies [92, 93], where signals of widely differing intensity appear, and broad feet from strong lines can obscure weaker signals.

Solid State Physics

Planar waveguide structures have been used extensively in solid state physics, including in experiments that relate directly or indirectly to magnetic resonance. For example, Yusa et al. have demonstrated the detection of nuclear spin states in GaAs by subtle effects of the nuclear magnetism on the conduction of photo-induced charge carriers [94] (cf also [95]). This allowed the detection of as few as 10^8 nuclear spins, which is a remarkable achievement even at the experimental temperature of 100 mK. Conducting microstrips have been deposited on top of a ferromagnetic layers in order to obtain broadband ferromagnetic resonance signals. In this way, the magnetic properties of thin film structures can be studied by inductive microwave spectroscopy [96, 97]. Similar techniques using optical detection have been described, as well [98].

Waveguides for Dynamic Nuclear Polarisation While optimised detector geome-

tries mitigate the inherently poor sensitivity of the NMR experiment, they do not ultimately address its root cause: the magnetic polarisation of nuclear spins is minuscule (order of 1 spin in 10^5), even at the highest practical magnetic fields. Sample cooling helps to an extent, but is undesirable for studying many systems, in particular in biology. Several methods are known to temporarily increase the nuclear polarisation above the thermodynamic equilibrium value, including parahydrogen-induced polarisation, optical pumping, and dynamic nuclear polarisation (DNP). Each of these approaches has its merits and limitations. Among them, DNP is of most interest in the present context, because it places high requirements on the resonator structure surrounding the sample. DNP transfers polarisation from the electron to the nuclear spins by cross-relaxation. Obviously, a radical species needs to be present in the sample, with suitable electron spin relaxation times. Stable nitroxide radicals are commonly used for this purpose. DNP requires saturation, or at least, significant perturbation, of the electron spin temperature by microwave irradiation. At typical NMR magnetic fields, this involves microwave frequencies up to several hundred GHz. Transporting microwave power in this part of the spectrum requires carefully designed waveguide structures. DNP tends to be most efficient in the solid state, particularly at cryogenic temperatures. This has led to the development of dissolution-DNP techniques [99], in which the sample is first cooled to 4K or even below, and then irradiated with microwaves for about an hour or so, and finally rapidly dissolved in a hot solvent, to be transferred to an NMR magnet for spectroscopy, or injected into a patient inside an MRI scanner for imaging. At small enough scale, it is possible to avoid the dissolution and the transfer step, and rapidly melt the sample in-situ after microwave irradiation by means of either an electric heater or exposure to a hot gas. This has been achieved recently by Sharma et al. [100]. A capillary of 360 μm outer diameter is moved between three regions inside an NMR magnet: a cold region at 77 K, where the sample is irradiated with microwaves, a hot region, where the capillary is exposed to a stream of warm nitrogen gas, and an NMR region, where the NMR spectrum is measured using a stripline resonator. DNP also works in the liquid state. However, the transfer tends to lose efficiency at high magnetic fields, and the penetration depth of microwaves at high frequency into most liquids at ambient temperature is very poor. Nonetheless, there is considerable interest in direct liquid-state DNP [101–103] due to its conceptual simplicity, and because it could potentially be applied to systems that cannot tolerate freezing and thawing. Liquid-state DNP systems are essentially electron-nuclear double resonance spectrometers, and require irradiation at both the nuclear and electron Larmor frequencies simultaneously at least in short succession. The design of suitable resonators is challenging, since the low-frequency structure tends to shield the sample from access to the high-frequency radiation. Annino et al [104–106] have designed a dielectric cavity microwave resonator combined with a waveguide radio frequency resonator based on a pair of straight wires, operating at a magnetic field of 3.3T. This corresponds to electron and proton Larmor frequencies of 95 GHz and 150 MHz, respectively. The microwave power is coupled in through a rectangular waveguide from a solid state source. At a microwave power of about 70 mW, an enhancement of the proton signal of -16 was observed in mixture of dioxane and water containing a nitroxide radical.

Another design has recently been presented by Denysenkov et al. [107–110] Their system operates at even higher frequencies, with a magnetic field of 9.2 T (392 MHz NMR / 260 GHz EPR frequencies). They employ a much more powerful gyrotron microwave source, which is coupled into the DNP system using a corrugated waveguide. The microwaves emanate from the waveguide into a Fabry-Perot resonator, the back (mirror) plane of which is formed by a stripline radio frequency resonator. The liquid sample forms a thin liquid film of 20 μm thickness and 50 nl volume directly on the conducting stripline surface. This ensures excellent thermal contact, and prevents the liquid from heating up too much upon microwave irradiation. The microwave power employed in Denysenkov's design is about two orders of magnitude stronger than in the one by Annino et al. Signal enhancements of up to a factor of 30 have been observed with this system.

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