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Perspectives in Magnetic Resonance

# Single spin magnetic resonance

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ABSTRACT

Different approaches have improved the sensitivity of either electron or nuclear magnetic resonance to the single spin level. For optical detection it has essentially become routine to observe a single electron spin or nuclear spin. Typically, the systems in use are carefully designed to allow for single spin detection and manipulation, and of those systems, diamond spin defects rank very high, being so robust that they can be addressed, read out and coherently controlled even under ambient conditions and in a versatile set of nanostructures. This renders them as a new type of sensor, which has been shown to detect single electron and nuclear spins among other quantities like force, pressure and temperature. Adapting pulse sequences from classic NMR and EPR, and combined with high resolution optical microscopy, proximity to the target sample and nanoscale size, the diamond sensors have the potential to constitute a new class of magnetic resonance detectors with single spin sensitivity. As diamond sensors can be operated under ambient conditions, they offer potential application across a multitude of disciplines. Here we review the different existing techniques for magnetic resonance, with a focus on diamond defect spin sensors, showing their potential as versatile sensors for ultra-sensitive magnetic resonance with nanoscale spatial resolution.



## 1. Introduction

Magnetic resonance, either as electron paramagnetic resonance (EPR) or as nuclear magnetic resonance (NMR), is one of the most abundant analytical and imaging techniques. Because it is sensitive to transitions between nuclear states, the attainable spectral resolution is without peer. EPR spectra often show resolution of hyperfine coupling to nuclei giving access to information on chemical composition, electron density and geometrical structure. NMR, on the other hand, shows unprecedented chemical specificity through analyzing chemical shift and *J*-coupling data. Nevertheless, both techniques are limited in sensitivity since they mostly rely on inductive interaction of spins with the detection device being a pickup coil in the case of NMR setups - which typically is challenged by thermal noise in the detection signal. More specifically, inductive detection is well suited to measuring large magnetic moments rather than single spins from basic geometric considerations. The inductive voltage signal through a surface is proportional to the time derivative of the magnetic flux flowing through it. The latter, in turn, is proportional to the number of magnetic flux lines that pass through a specific surface. If one considers a sample inside a pick-up coil then the inductive signal will only be generated by those field lines closing outside the loop. Given a certain loop size, the magnitude of the signal will decrease with shrinking sample size. For a single spin the inductive signal will thus be drastically reduced unless the loop size is reduced at the same time. Since loop sizes below a few tens of μm are limited by self-induction, no single spin detection is feasible with this technique. The state-of-the-art in sensitivity of NMR with micro coils is around $10^{13}$ spins/$\sqrt{\text{Hz}}$ [1].

As a result, several methods have been developed, enabling the detection of very weak magnetic resonance signals with the aim of achieving single spin detection. The three most prominent magnetometry methods, namely atomic vapor cells, superconducting quantum interference devices (SQUIDs) and magnetic resonance force microscopy (MRFM) will be briefly reviewed below.

Atomic vapor cells are one of the most sensitive detection methods for magnetic fields, achieving sensitivities as high as $10^{-18}$ T/$\sqrt{\text{Hz}}$. This makes them ideal for a number of applications in NMR detection. The magnetic field measurement principle is based on the Faraday effect in a vapor of alkali atoms such as K, Rb or Cs - confined in an optically transparent cell close to the specimen to be measured. The atoms of the alkali vapor are optically polarized via a circularly polarized pump beam. In

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the presence of the magnetic field to be measured, generated by, for example, an ensemble of nuclear spins, the alkali atoms start to precess with a frequency corresponding to their gyromagnetic ratio. Using a linearly polarized probe beam, one can detect an NMR signal via a tilt of the probe beam polarization. The tilt is based on the Faraday rotation which is directly proportional to the strength of the external magnetic field. As a result, vapor cells are quite bulky in size. In order to maintain appropriate vapor densities and long $T_1$ times of the alkali spins one has to use vapor cells in the range of $cm^3$. A sensitivity for proton spins in a volume of around 1 $mm^3$ was estimated [2] to be $\sim 10^{13}/\sqrt{\text{Hz}}$.

SQUIDs comprise a superconducting ring interrupted by two Josephson junctions, e.g. insulating barriers. Due to quantum interference only a current which is periodic in the magnetic flux penetrating the ring can flow in the ring. In d.c. SQUIDs, a d.c. current is running through the ring - this generates a voltage drop across the junction which changes in the presence of the induced currents. A change in magnetic field, caused by driving the spin transition of sample spins, can thus be directly detected electrically. SQUIDs are considered one of the most sensitive methods for detecting a magnetic field flux, reaching a noise floor of 0.33 $\text{fT}/\sqrt{\text{Hz}}$ for a loop diameter of a few mm [3]. Because the SQUID needs to be kept at cryogenic temperatures, measurements usually take place at low temperature as well. There are, however, examples for measurements with samples at room temperature [4], although there sensitivities usually are not better than standard NMR. With nanoSQUIDs [5], on the other hand, the projected electron spin sensitivity reaches unity [6], which could translate to approximately $10^3/\text{Hz}^{1/2}$ for nuclear spins.

One of the most promising methods for magnetic resonance detection at the nanoscale is MRFM. This technique uses a magnetic tip, attached to a small mechanically resonant cantilever and placed above a spin containing sample. A nearby RF coil generates a resonant alternating field. The magnetic tip generates a magnetic field gradient, which extends into the sample volume. Just like in conventional magnetic resonance imaging (MRI) the magnetic field gradient encodes spatial information in the recorded resonance. To enhance sensitivity, experiments are carried out at cryogenic temperatures, at which the thermal fluctuations, especially of the cantilever, are greatly suppressed. In the presence of the static magnetic field $B_0$ and the inhomogeneous magnetic field generated by the magnetic tip, a specifically chosen RF frequency addresses sample spins inside a restricted sample volume (resonance slice) meeting the resonance condition. During the experiment the cantilever is oscillating above the sample while applying the alternating field. This induces periodic spin flips inside the sample which in turn exert a magnetic force onto the magnetic tip - the concomitant slight shift of the cantilever frequency is then read out. In an inverted geometry the sample is attached to the tip of the cantilever and is scanned across a static magnetic tip. In that geometry the sample is essentially moved back and forth through the resonance slice. With this detection method, sample volumes as small as $(4\,\text{nm})^3$ with an effective number of around 100 nuclear spins have been detected [7]. MRFMs need to operate at cryogenic temperatures, too.

Technological advances in magnetometry have brought forth new magnetometers with very high sensitivity, which makes it possible to measure very small magnetic fields. On the nanoscale, magnetic fields have dipolar characteristics as they originate from single electron and nuclear spins. The strength of these fields scales like sample-detector distance, $1/r^3$. As a result, detectors on the size of the field origin itself, e.g. single atoms, are best suited to capture single electron and nuclear magnetic fields. So far, only miniaturized SQUIDs [6,8] and magnetic resonance force microscopes [7] have exhibited few-spin magnetic field sensing with nanoscale resolution. Nevertheless, their challenging experimental requirements, with emphasis on temperature and vacuum, calls for novel sensor types.

## 2. Diamond defect spin sensors

Sensing magnetic field with spins is a prevalent technique. Sensitive NMR probes to measure fields are common techniques for a number of applications including field stabilization of NMR and EPR spectrometers themselves. Typically, the accuracy reached is in the order of a few parts per million (ppm) with fields ranging up to 20 T, i.e. 10 $\mu\text{T}/\sqrt{\text{Hz}}$. This is equivalent to the field of a single electron spin at a distance of 1 μm. Despite their reasonable sensitivity, such spin probes are not sensitive enough to measure single electron spins since their size is on the order of a few $cm^3$. As a result, spin sensors need to be small without compromising their sensitivity for single spin detection. Ultimately, such sensors contain a single spin themselves and can be brought into close proximity to the sample. The sensitivities of the different techniques presented in Section 1 are plotted in Fig. 1. In the past, several systems have been identified with the potential of detecting single spins in solids. Nearly all of those have been obtained via a combination of optical measurement and spin resonance. Specifically the first such optically detected magnetic resonance experiments were done on single molecules at low temperature, basically combining single molecule spectroscopy and electron spin resonance [10]. These early experiments relied on the existence of an excited metastable triplet state, the lifetime of which depends on the specific spin state. Spin Rabi oscillations as well as spin coherence was measured [10–12] and for the first time ideas of using single molecules as sensitive and highly local magnetic field probes were conceived [13]. Yet, as the spin carrying state is an excited state with limited lifetime, sensitivity as well as versatility is greatly reduced. Few systems are known, which have a paramagnetic ground state and at the same time show strongly allowed optical transitions. Among those are quantum dots [14] and defect centers in solids [15,16]. Certain materials, most notably diamond and sil-

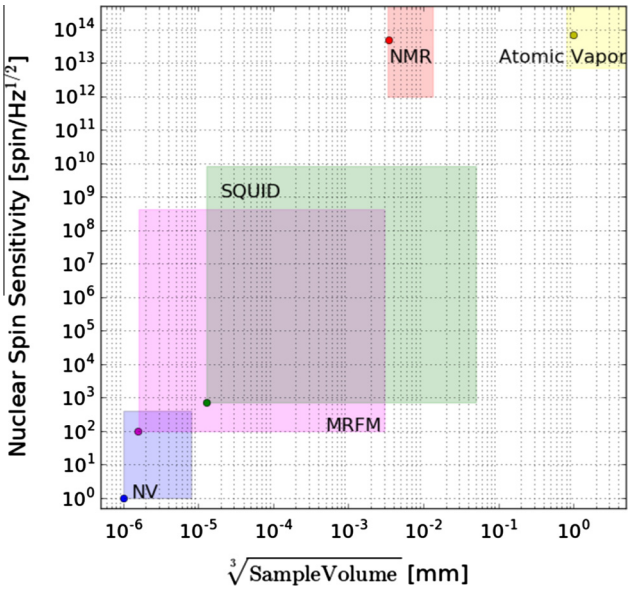


**Fig. 1.** Nuclear spin sensitivity for different sensing techniques plotted against their typical sensing volume: microcoil NMR [1], atomic vapor [2], SQUID [6], MRFM [7] and the NV center in diamond [9]. The rectangles serve as guide to the eye, depicting the space each techniques approximately covers, with the rounds markers setting the current state-of-the-art of each one.