Quantum metrology with single spins in diamond under ambient conditions

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ABSTRACT

The detection of single quantum systems can reveal information that would be averaged out in traditional techniques based on ensemble measurements. The nitrogen-vacancy (NV) centers in diamond have shown brilliant prospects of performance as quantum bits and atomic sensors under ambient conditions, such as ultra-long coherence time, high fidelity control and readout of the spin state. In particular, the sensitivity of the NV center spin levels to external environmental changes makes it a versatile detector capable of measuring various physical quantities, such as temperature, strain, electric fields and magnetic fields. In this paper, we review recent progress in NV-based quantum metrology, and speculate on its future.

Keywords: diamond, nitrogen-vacancy centers, quantum metrology, quantum sensing, quantum information process

INTRODUCTION

Magnetic resonance is an established technique to obtain non-destructively information about molecular structure, including biomolecules [1]. On the other hand, the technique also has wide applications in quantum control and imaging. Recently, magnetometers based on diamonds [2–5] and magnetic resonance force microscopy [6–8] have been demonstrated using magnetic resonance on nanoscale spins with ultra-high sensitivity [9].

The nitrogen-vacancy (NV) center in diamond is one of the most promising magnetic resonance systems. The excellent features, including optical readout, optical polarization [10] and coherence time of milliseconds [11–13], make the system an important tool in quantum information processing and quantum metrology. Since scientists from the USA and Germany proposed nanoscale magnetic imaging under ambient conditions in 2008 [14–16], NV centers have been rapidly progressing in quantum metrology. NV centers have been used as interferometers to measure magnetic fields, electric fields [17] and temperatures [18–20] at the nanoscale. In particular, the magnetic-field measuring precision has been improving to realize external single-nuclear-spin readout, which is a prerequisite of NMR-based single-molecule imaging.

This review is organized as follows. In the first section (NV CENTER) we recapitulate the structure and Hamiltonian of the NV center. In the second section (MAGNETOMETRY) we give a concise introduction to the principle and typical sensitivities of the detection of magnetic fields using the NV center in the first subsection (Nanoscale magnetometry) and then the second subsection (Sensing spins) highlights vital progress on nanoscale electron spin resonance (ESR) and nuclear magnetic resonance (NMR). Other metrology applications such as electrometry and thermometry are discussed in the third section (OTHER METROLOGY).

NV CENTER

Structure

An NV center is composed of a nitrogen impurity and an adjacent vacancy, as shown in Fig. 1(a). The structure has $C_{3v}$ symmetry with the 'nitrogen-lattice vacancy' pair oriented along the axis of symmetry, normally called the NV axis. The Fermi level of the diamond lattice makes the NV center prefer to be negatively charged, NV$^-$, or neutral, NV$^0$ [21,22]. In particular, it is convenient to polarize and read out the spin state of an NV$^-$ by
Figure 1. (a) The structure of an NV center; (b) the electronic energy level structure of NV− [23].

applying a 532 nm green laser, due to an intersystem crossing process. This makes NV− promising in quantum computation and quantum metrology. Hereafter, the NV− center is denoted as NV without a specific description.

The electron energy levels of the NV are shown in Fig. 1(b) [23]. The ground state 3A2 and the first excited state 3E are electron-spin triplet states; 1A1 and 1E are electron-spin singlet states. The zero-field splitting of 3A2 into mS = 0 and mS = ±1 states of 2.87 GHz characterizes NV−. The fluorescence intensities of NV− are spin-dependent on its original states before the laser illumination, which enables the readout of its spin state. The principle of the spin-dependent fluorescence is sketched in Fig. 1(b), with radiative transitions and non-radiative ones denoted as solid lines and dotted lines, respectively. The mS = ±1 sublevels in the 3E excited state have a higher probability of decaying non-radiatively to the ground state mS = 0 via singlet states, while the mS = 0 sublevels of the excited state are more likely to experience a spin-conservation process by radiating a single photon and decaying to the ground state. As a result, the mS = ±1 spin states have a weaker fluorescence intensity and the population will be pumped to mS = 0 after repeated pumping, resulting in high spin-polarization (92% population on the mS = 0 state) in a few microseconds even at room temperature.

The Hamiltonian of an NV center

The Hamiltonian of the ground state of an NV center is

\[
H = DS^2 + E \left(S^2_x - S^2_y\right) - γ_eB \cdot S + S \cdot \sum_i A_i \cdot I_i,
\]

where the z direction is along the NV axis. Here D = 2.87 GHz is the zero-field splitting of the electron spin at room temperature but varies linearly with temperature [24], which makes the NV center a temperature sensor [18–20]. The second term is the off-diagonal term of the zero-field splitting. In an ideal lattice without an external electric field, E = 0; when a horizon stress or electric field is present, E ≠ 0. So the stress and the electric field can be measured by the effect of E [17]. It is noted that E is also temperature-dependent [24]. The third term is the Zeeman term, describing the interaction of the magnetic field B with the electron spin, which enables the NV center for magnetometry. The last term describes the interaction of the electron spin of the NV with other spins, such as the nitrogen nuclear spin nearby, and the nuclear and electron spins in the environment. This term can be manipulated to detect and control other spins. The applications of each term in the Hamiltonian are summarized in Fig. 2.

MAGNETOMETRY

Nanoscale magnetometry

As the magnetic field generated by magnetic moments decreases with distance (inverse cubic dependence), the further away is the probe detector from the spins that carry the magnetic moments, and the higher is the magnetic field sensitivity required for the probe detector. So far, Hall detectors, traditional NMR, SQUID, atom gas units, magnetic resonance force microscopy, NV centers and so on have been used to probe magnetic field signals. Their sensitivities and spatial resolutions are schematically shown in Fig. 3 [26]. Normally, a sensitivity of 1 μB/Hz−1/2 (Bohr magneton) is required to probe a single electron spin and ~1/1000 μB/Hz−1/2 [27] for a single proton, which can be hopefully achieved using NV centers.

The idea of the NV center as a magnetic field probe arose in 2008, when Wrachtrup’s group [14] and Lukin’s group [15,16] demonstrated initial experiments for nanoscale magnetic field imaging with NV centers. A general scheme is shown in Fig. 4 [28]. The NV electron spin is polarized by a laser and then prepared to a superposition state with a π/2 microwave pulse. Different base states of the NV spin will accumulate different phases as a result of interacting with the magnetic field or detecting the spin evolving along different paths. The value of the phase depends on the strength of the interaction and the accumulation time. The phase information is then transformed, by making the two paths interfere with a π/2 pulse, into the population of an NV spin state, which can be read out optically. In ideal situations,
H = D · S_x^2 + E · (S_y^2 − S_z^2) − γ B · S + S · ∑ A_i · I_i

\( \delta B \approx \frac{\hbar}{2\pi g \mu_B \sqrt{T_1 T}} \)

where \( T_1 \) is the coherence time of the NV’s electron spin state, \( T \) the time of one measurement, which is limited by \( T_2, \mu_B \) the Bohr magneton, \( \hbar \) the Planck constant and \( g \approx 2 \) the Landé factor of the electron spin. In principle, \( 1 \mathrm{nTHz}^{-1/2} \) sensitivity can be achieved given a \( T_1 \) value of \( 0.1 \sim 1 \) ms, which is typical for NV centers in bulk. Moreover, the size of the NV center probe can be set to 10 nm, which is not feasible with traditional methods.

In AC magnetic field detection, to improve the signal-to-noise ratio (SNR), dynamical decoupling technologies are used to prolong the coherence time, which will increase the signal accumulative time. However, in DC detection, dynamical decoupling technologies have no effect, and as a result, the detection time is limited by \( T_1^* \). Conventionally, space resolution is sacrificed in an ensemble magnetometer to improve SNR [29,30]. In addition, in order to achieve a sensitivity of \( f \mathrm{THz}^{-1/2} \) with millimeter resolution, multi-qubit entanglement schemes have been proposed [31–33].

Many applications of NV-based magnetic sensing techniques have been proposed and demonstrated ever since, such as the magnetic imaging using an array of spins in diamond in 2010 [34], the nanoscale imaging accomplished by combining a single nitrogen vacancy with atomic force microscopy (AFM) [35], the sensing of a mechanical resonator in 2012 [36], the sensing of a static vector magnetic field in 2013 [37], and the vector microwave magnetometry based on a single nitrogen-vacancy center in diamond in 2015 [38]. It is especially worth mentioning that the method can be applied to probe oscillating magnetic fields with frequencies ranging from kHz [15] to GHz [38]. Furthermore, Du’s group implemented high-resolution vector microwave magnetometry [38] based on the Rabi oscillation of NV spins driven by a resonant microwave magnetic field. The magnetic field vector can be reconstructed by utilizing NV centers of four different orientations.

**Sensing spins**

Using nitrogen-vacancy centers to sense near-surface external electron spins began in 2011 [39]. Its principle has been demonstrated by three groups [40–42] and the sensing of an external single electron spin was achieved in 2012 [43]. In 2013, two groups [2,3] simultaneously reported the realization of microscopic NMR at nanoscale using an NV center as a probe to detect the proton NMR signal in an organic sample outside of the diamond. Then sensing and atomic-scale structure analysis of single-nuclear-spin clusters in diamond were demonstrated [44]. Recently, NMR on four \(^{28}\)Si spins with single-nuclear-spin sensitivity was performed [27]. Moreover, detection of electron spin resonance spectra from a single protein was...
achieved [5], making it possible to extract structure and dynamics information [45] from a single biomolecule even in living cells. Details of several recent works will be discussed below.

Nano-ESR

In diamond there are numerous defects with electron spins not directly detectable via photoluminescence, which are called dark spins [46]. Initializing and reading out a dark electron spin provides a verification of the feasibility of sensing an external single spin and the possibility of using the dark electron spins as local quantum registers [47].

To detect a single electron spin, two protocols of spin-echo-detected double electron–electron resonance (known as SEDOR or DEER [3,48–50]) are applied. The basic scheme is shown in Fig. 5(a). The dark spin produces at the NV center a magnetic field ΔB, which superposes the noise magnetic field at the NV center produced by the spin bath. The NV center spin will accumulate different phases as a result of its interaction with the magnetic field. When a π operation of the NV center is inserted in the middle of the precession time, the phases accumulated during the two τ periods cancel each other. But when an RF is inserted in the Hahn echo pulse sequence to flip the dark spin simultaneously with the NV center spin, the phase induced by the dark spin will be accumulated for the whole time. As a result we can obtain information on the dark spins. Figure 5(b) shows that tuning frequencies equal to the coupling strengths appear when we fix the RF pulse as a π operation and change the time τ gradually.

Single-molecule ESR. Nanoscale ESR outside diamond has been achieved in recent years. In 2013, detection and nanoscale imaging of the magnetic field produced by a single NV center were achieved [43]. Several groups attempted to sense the nitrogen-oxide spin labels attached to the diamond [39,48]. However, none of them successfully observed the three characteristic hyperfine peaks of the nitrogen-oxide label. This indicated that the signal was from the surface radicals rather than the nitrogen-oxide spin labels.

3D imaging and structure analysis of single biomolecules have been pursued by several researchers [39,43,48,51]. One critical step was achieved in 2015 by Du’s group [5]. They chose the MAD2 (mitotic arrest deficient-2) protein as the sample. This protein was easily site-specifically modified with a single nitroxide spin label and immobilized on the diamond surface by embedding it in a polyllysine layer. The detection was based on the magnetic dipole interaction between the spin label and a single NV center [52].
Figure 6. Quantum logic cooling of the dark spin. (a) Cooling sequence. (b) Gates implemented by a modification of the SEDOR sequence. (c) Evolution of the NV center over the e-CNOT gate in (b). (d) Result of sequence (a). Reprinted with permission from [47].

Figure 7. Diagram of the setup, experimental method and pulses for the single-molecule ESR experiment [5]. (a) On the surface of diamond, MAD2 proteins labeled with nitroxide spin labels; under the surface of diamond, NV centers were implanted. Microwaves were applied by a coplanar wave guide. (b) AFM image for freeze-dried proteins on the diamond surface. (c) Pulse sequence to measure the coupling of an NV sensor to the protein. Reprinted with permission from [5].

NV centers were about 5 nm below the surface of the diamond and the size of the spin label was much smaller than a single MAD2 molecule (∼5 nm), which was ensured by AFM as shown in Fig. 7(b). The experimental pulses to measure the coupling between an NV center and the protein are shown in Fig. 7(c). Periodic XY8-N pulses on the NV center were used to preserve the NV sensor’s coherence and to increase its sensitivity in the magnetic field, while RF pulses were applied on the nitroxide spin labels to flip the electron spins synchronously.

The ESR spectrum of a single spin label is shown in Fig. 8(a). The three peaks mark the hyperfine interaction between the spin label’s electron spin (S = 1/2) and the nitrogen nuclear spin (I = 1) at an external magnetic field B0 = 153.0G. The ensemble ESR spectrums in fluid (Fig. 8(b), upper panel) and frozen (Fig. 8(b), lower panel) solutions are shown in Fig. 8(b). In principle, the spectrum of a single spin label is closer to the solid-state spin ensemble (Fig. 9(b), lower panel) in which the random orientation of the molecular spin principal axis causes the broadening of the spectral peaks [53]. This reveals that the anisotropic hyperfine coupling can be determined reliably through single-spin ESR. The significance of obtaining the structural and dynamical information is shown below.

Close analysis of the spectra (Fig. 9) reveals the molecular dynamics. Figure 9(b) shows that the transition frequencies depend on Φ. The molecular motion specifically changes the angle between the nitrogen π orbitals (ZM in Fig. 9(a)) and B0, which causes the broadening of the peaks (Fig. 9(c)). The asymmetric peaks become more obvious as the external magnetic field increases (Fig. 9(d)). The electron g-factor is consistent with the reported values [54].

Figure 10(a) shows the DEER sequence for deriving the relaxation time of the spin label and its coupling strength to the NV center. Figure 10(b) shows the simulations for different spin relaxations and coupling strengths. The possible sites of spin labels in the transverse cross section constrained by the coupling strength are denoted by red lines in Fig. 10(c). As a result, they derive a coupling strength of 90 kHz corresponding to a distance between the spin label and the NV spin of ∼9 nm. The size of the spin label is much smaller than a single MAD2 molecule (∼5 nm), which is important for single protein detection.

Addressing single-electron spin labels on proteins enables ultra-precise structure determination based on NV centers. It extends the sensing range to dozens of nanometers, while diamond-sensor-based NMR [2,3,27,44] can only sense nuclear spins in very close proximity.

Nano-NMR

Detecting a single 13C has been implemented through measuring the decoherence of NV centers by applying dynamical decoupling [40–43]. In 2012, Du’s group detected a single 13C–13C pair about 1 nm away from the NV sensor by using the multiple dynamical decoupling sequences on the NV center and obtained the
coupling strength between two nuclear spins by analyzing the experimental data [44]. Based on the coupling strength, the orientation of the spin pair in atomic-scale resolution can be resolved. In the NV center’s eigenstates $|m_S = 0, +1 \rangle$, the Hamiltonian of the system containing the NV center and the $^{13}$C–$^{13}$C dimer is [55,56]:

$$H = \omega_C |0\rangle \langle 0| + \omega_1 |+1\rangle \langle +1| + |+1\rangle \langle +1| \otimes (A_1 \cdot I_{1z} + I_{1z} + I_{2z})$$

(2)

$\omega_C$ is the Zeeman frequency of the nuclear spins, $A_{1,2}$ are coupling between nuclear spins and NV center spin state $| +1 \rangle$, $D_{1,2}$ is the dipolar coupling tensor between nuclear spins $I_1$ and $I_2$. The dynamical evolution of the dimer can be described by the pseudo-spin model. Two spin states of the dimer $|--\rangle$ and $|--\rangle$ map to the pseudo-spin states $|\uparrow\rangle$ and $|\downarrow\rangle$; the other two states of the dimer $|--\rangle$ and $|--\rangle$ can be ignored due to the fact that their Zeeman splittings are much larger than the coupling strengths under a high magnetic field, which will not induce evolution in coupling interaction. The Hamiltonian of pseudo spins is described [55]:

$$H^{(m_S)} = \frac{1}{2} J^{(m_S)} \cdot \sigma = \frac{1}{2} (X \sigma_x + Z^{(m_S)} \sigma_z)$$

Here, the pseudo spin affected by the effective field $J^{(m_S)}$ decomposes to $X$ and $Z^{(m_S)}$, which are the coupling strengths between the two spins and the difference of coupling with the NV, respectively.

Under the effective field, the dimer begins to evolve between the two pseudo-spin states periodically, which will induce a periodic magnetic field on the NV center. By applying dynamical decoupling sequence pulses, the dimer’s information can be obtained through measuring the accumulated phase generated by the effective magnetic field.

Nanoscale proton MR. In 2013, scientists from China and Germany worked together to perform an experiment to detect proton signals in liquid and solid organic samples with a volume of $(5 \text{ nm})^3$ [2]. In this work, the proton signals from the liquid and solid on the surface of diamond were achieved by using an NV center as a sensor. The Larmor precession of the protons under an external magnetic field would generate fluctuation signals of amplitude and phase. The dynamical decoupling pulses XY8-N were used to detect the spin noise. A Ramsey interferometer consisting of a $\pi/2$ pulse at the beginning and the end of the sequences was used to detect the magnetic noise. The $N \pi$ pulse amplified the noise at some specific frequencies while suppressing it at others frequencies; i.e. it acted like a filter. The spin noise spectrum can be measured by modifying the pulse evolution time $\tau$.

Combined with the scanning NV probe technology, it is hoped that nanoscale-NMR imaging applications will be implemented [14,35]. NMR detection can be achieved at a low, even zero, magnetic field as the signals come from statistical polarized nuclear spins instead of traditional thermal polarized signals [57]. In this principle, instead of rotating the sample in the normal magic angle spinning technique, we can actually rotate the external magnetic
field, which means that it is easier to achieve higher rotating speeds. This has important applications in solid NMR. It can also be extended to hyperpolarization applications via coherent transferring of the polarization from the NV center to nuclear spins.

**Single-spin-sensitivity NMR.** In 2015, scientists from Germany and China performed the detection and imaging of near-single nuclear spin outside the diamond. In their reports, four silicon nuclei were detected on the diamond. They realized strong coupling between the NV sensor and nuclei by exploiting the field gradient generated by the diamond. The scheme of the experiment is shown in Fig. 11(a). Amorphous silica was deposited on the diamond surface, which had shallow NV centers of 2–3 nm in depth. Strong coupling was obtained by using a diluted spin sample as $^{29}$Si nuclear spins at the surface experience a dipolar magnetic field from nearby NV centers; this was stronger than the inter-nuclear coupling, exceeding even the coupling between $^{28}$Si dimers (Fig. 11(b)). The signal measured by the XY8 spin-echo sequence is plotted in Fig. 11(c, d). The clear dip near the $^{29}$Si

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**Figure 10.** Sequence and distance between the NV center and the spin label. (a) DEER sequence between an NV center and a spin label. (b) Simulations of different spin label relaxations and coupling strengths. (c) The possible sites of the spin label in the transverse cross section containing the NV center vector illustrated by red lines. Reprinted with permission from [5].

**Figure 11.** $^{29}$Si nuclei NMR with a strongly coupled sensor. (a) Schematic of the setup. (b) Schematic of the strong coupling regime. (c) Using the XY8-K decoupling sequence to measure the $^{29}$Si NMR signal as a function of the applied magnetic field. Reprinted with permission from [27].
Larmor frequency resulted from the relative phase acquired by the NV center. The NMR signal with inhomogeneous broadening became apparent, as shown in Fig. 12(a). The spectral decomposition of the contributing nuclear spins and their hyperfine coupling parameters implied that four nuclei account for more than 50% of the signal. Basis pursuit de-noising (BPDN) recovered the best fit locations of the silicon nuclei to present how structural information and imaging may be obtained. The ultimate sensitivity limit of NMR spectroscopy was achieved there by the signal-to-noise ratio of the experiments, as shown in Fig. 12(b). This work showed that the sensitivity of NMR and imaging can be extended to single nuclear spins in the strong coupling regime.

### OTHER METROLOGY

**Vibration**

As described above, by applying the dynamical decoupling pulse sequence, sensing of the AC magnetic field signal can be achieved by detuning the coherent curve. The signal also results from spin precession or other vibration of the magnetic material. For instance, the vibration of the mechanical resonator can be detected by measuring the vibration of the magnetic field at the NV center nearby. This was done by a group in the USA in 2012 [36].

When the resonator is far from the NV center, the field gradient at the NV center is so small that it is not enough to generate an obvious signal by the Brownian motion of the resonator. Driving the cantilever strongly will induce magnetic field oscillations, so that the frequency and average displacement can be analyzed. When the distance between the cantilever and the NV center is short enough, the oscillating field will be detected by the NV center as a result of the large gradient field. In this method, the Brown motion of the cantilever can be measured. By further developing the techniques, the zero-point oscillation might be detectable by the NV center and so strong coupling between single phonons and spins might be realized.

**Electrical field**

Detecting a single charge is significant in many research fields and applications. In contrast to other methods of detecting a weak electric field, the NV center electric field transducer works in ambient conditions with atomic spatial resolution [17]. Because of the spin–orbit coupling between the ground state and the excited state, the NV center has an electric dipole moment at the orbital ground state. The energy difference of the \( m_S = 0 \) and \( m_S = \pm 1 \) states is sensitive to the electric field when the static magnetic field is perpendicular to the NV center axis. The AC electric field sensitivity has reached 202 \( \pm 6 \) V cm\(^{-1}\) Hz\(^{-1}\), corresponding to the electric field produced by a single charge about 150 nm away. Although this value is two orders of magnitude off relative to the most sensitive method, the nanoscale sensor can be much closer to the detected charges. Thus the possibility to image individual charges with nanometer spatial resolution under ambient conditions is opened up.

**Temperature**

In 2010, the dependence of the zero-field splitting and temperature of NV centers was obtained as \( dD/dT = -74.2(7)\) kHz/K [24]. This makes
NV centers highly sensitive temperature probes of nanometer spatial resolution.

The sensitivity of NV-center-based thermometry reached 25 mK/√Hz [19] and 5 mK/√Hz [18]. The signal was only related to $D$ and the phase-accumulating time. This was achieved by state swap between $m_S = +1$ and $m_S = -1$ during the phase-accumulating period, thus eliminating the low-frequency magnetic noise. Furthermore, nanoscale thermometry in a living cell has been demonstrated [20]. As a temperature transducer, the NV center has three merits: (i) ability to be implanted into the cell or the body without fatal damage; (ii) ability to be read out through the laser without interference from other electromagnetic noise; and (iii) the fact that the average laser readout power can reach hundreds of microwatts without damaging the sample activity.

**Other schemes**

As the understanding of the NV center becomes deeper and quantum control techniques improve, other promising precision metrology schemes based on NV centers have been proposed, e.g. a quantum gyroscope, depending on magnetic field measurements [58,59], and a portable precision clock instead of an atomic clock [60]. The measurement resolution enhancement can also come from quantum entanglement: squeezing [61]. In the future, detecting and analyzing techniques based on NV centers will give rise to significant improvements in metrology.

Apart from the application in quantum metrology, the NV center is widely applied in many other fields such as quantum information processing [62], hybrid quantum circuits [63] and quantum memory [64].

**CONCLUSIONS**

Quantum metrology lays the foundation for new discoveries and new technologies. Developments of quantum systems for quantum metrology will improve our understanding of the quantum world. Quantum metrology based on NV centers breaks through the limits of typical magnetic resonance techniques and covers the measurements of many physical quantities including time, force, heat, electricity and magnetism, opening up vast applications in physics, chemistry, biology and materials science. With the mechanisms becoming clearer and clearer and the development of superb controlling techniques, further research will increase the range of applications and make them more feasible.

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