Submillihertz magnetic spectroscopy performed with a nanoscale quantum sensor

Simon Schmitt,1 Tuvia Gefen,2 Felix M. Stürner,1 Thomas Unden,1 Gerhard Wolf,1 Christoph Müller,1 Jochen Scheuer,1,3 Boris Naydenov,1,3 Matthew Markham,4 Sebastien Pezzagna,5 Jan Meijer,5 Ilai Schwarz,3,6 Martin Plenio,3,6 Alex Retzker,2 Liam P. McGuinness,1,6 Fedor Jelezko1,3

Precise timekeeping is critical to metrology, forming the basis by which standards of time, length, and fundamental constants are determined. Stable clocks are particularly valuable in spectroscopy because they define the ultimate frequency precision that can be reached. In quantum metrology, the qubit coherence time defines the clock stability, from which the spectral linewidth and frequency precision are determined. We demonstrate a quantum sensing protocol in which the spectral precision goes beyond the sensor coherence time and is limited by the stability of a classical clock. Using this technique, we observed a precision in frequency estimation scaling in time $T$ as $\propto T^{-3/2}$ for classical oscillating fields. The narrow linewidth magnetometer based on single spins in diamond is used to sense nanoscale magnetic fields with an intrinsic frequency resolution of 607 microhertz, which is eight orders of magnitude narrower than the qubit coherence time.

Quantum sensing and metrology exploit physical laws governing individual quantum systems or correlations between systems to perform detection at the limits of sensitivity, resolution, and noninvasiveness. In general, the techniques proceed by subjecting a quantum coherent probe to a Hamiltonian $H(t)$ that alters the evolution of the probe state over a duration limited by the probe coherence time $T_2$. A measurement is then performed to gain information about $H(t)$, such as its amplitude (Fig. 1A). As a result, the probe coherence time sets a limit on sensor performance because this is the maximum time over which coherent signal accumulation may be obtained. Subsequent measurements up to a total time $T$ may also be performed in order to improve the parameter estimation. For a single measurement with a sensor with long coherence time, a “Heisenberg” $1/T$ scaling in the precision of amplitude estimation can be obtained (7). However, most algorithms achieve a precision that scales as $1/\sqrt{T}$, resulting in sensitivity improving as $\sqrt{Hz}$ (2–6).

In addition to determining amplitude components, quantum spectroscopy aims at reconstructing the frequency spectrum of a given Hamiltonian as faithfully as possible. This task is of interest in, for example, chemical analysis, molecular structure determination, and microwave spectroscopy. The current gold-standard techniques focus on adjusting the system Hamiltonian during the interaction period in order to isolate individual frequency components. Referred to as dynamical decoupling, such techniques involve coherently pulsing or driving the sensing qubit, resulting in the generation of a spectral filter with linewidth given by the inverse of the interaction time (Fig. 1B) (7–9). The sensor linewidth is a critical figure of merit for spectral analysis because this defines not only the precision with which an individual frequency component can be estimated but also the ability to resolve several frequencies. As for amplitude estimation, square root precision scaling is observed for frequency estimation, albeit with appreciable overhead because of the need to sequentially sample different frequencies when obtaining a complete spectrum (Fig. 1, B and C).

Recently, the first approaches to reach a frequency resolution beyond the phase coherence time of the sensor qubit were performed. The protocols operated by transferring the quantum phase of the sensor to state population, which survives up to longer $T_1$ relaxation times ($10, 11$), or using a hybrid quantum system in which an additional long-lived qubit acts as a more stable clock (12–16). These techniques effectively replace the coherence time of the sensor qubit $T_2$, with the lifetime of a memory qubit $T_{2s}$. A drawback of this technique, however, can be that the overall sensitivity is reduced when the memory time greatly exceeds the sensing time because less time is spent acquiring a signal.

Here, we introduce a quantum spectroscopy technique in which the spectral resolution is independent of the sensor coherence time and an enhanced precision scaling of $T^{-3/2}$ is obtained. The technique is analogous to classical heterodyne detection in that an unknown signal is “mixed” with a local oscillator; however, in our protocol the nonlinear mixing element is a quantum coherent probe. This quantum heterodyne (Qdyne) detection scheme retains critical elements of both conventional heterodyne detection and quantum sensing to form a hybrid quantum-classical device that outperforms each technique in isolation. It is also distinguishable from “lock-in” techniques in that no feedback is required to lock the sensor to the signal phase (7). In particular, the frequency resolution of Qdyne is defined by the local oscillator stability, enabling the measurement linewidth to be narrowed beyond the $T_2$ limit of the quantum sensor. Unlike conventional heterodyne detection, however, the sensitivity is independent of the local oscillator intensity and is derived purely from the quantum sensor.

These properties can be seen by analyzing the interaction of a spin qubit with an oscillating magnetic field of the form $H(t) = kA\sin(2\pi vt + \phi)$, where $k$ is the interaction strength, $A$ is the Pauli spin-$\sigma$ operator, and $\phi$ is an arbitrary phase of the sensor magnetic field. Accumulation of a relative phase between two of the sensor’s spin levels—denoted here as $|0\rangle$, $|1\rangle$—after being brought into a coherent superposition state $1/\sqrt{2}(|0\rangle + |1\rangle)$ can be tailored to depend not only on the amplitude and frequency of the detected field but also on the signal phase with respect to the start of the measurement (Fig. 2). Specifically, for a decoupling sequence where $\pi$-pulses are applied with time separation close to $1/2\nu$, the sensor acquires a net phase $\Phi = \frac{\pi k}{\hbar} \cos(\phi)$, where $T_\pi$ is the interaction time (7, 17). Usually, no emphasis is placed on the signal phase because the detection is repeated many times and thereby averaged over all realizations (6). The idea we present here is to show that under the conditions, the signal remains coherent across multiple measurements, and the output state of the sensor depends on the signal phase $\phi$; then, control over the timing of subsequent experiments with a stable oscillator can be used to imprint changes in the signal phase onto the sensor. As a result, even though the sensor is reset after each measurement, correlations across measurements for times exceeding the sensor coherence time can be observed. The sensor phase $\Phi_N$ at each measurement time $T_N = nT_{1s}$ is then $\Phi_n = \frac{\pi k}{\hbar} \cos(2\pi n(T_\pi - T_{1s}) + \phi)$, where $T_{1s}$ is the sum of the interaction time and the readout time, and $\delta = \nu - \nu_{LO}$. Where $\nu_{LO}$ is a function of $T_\pi$ (Fig. 3A) (17). With knowledge of $T_{1s}$, a measurement of the beat frequency $\delta$ allows $\nu$ to be determined with an accuracy determined by the local oscillator stability and up to a sign ambiguity. The amplitude of the beat note, and thus the sensitivity, is proportional to


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the sensor phase accumulation, which is set by $T_s \leq T_2$. We used a photon correlation technique that allows frequency components fluctuating at time scales of several megahertz to be sampled, even though high-fidelity readout of our sensor requires several thousand measurement repetitions taking $\approx 1$ ms (17).

We demonstrate Qdyne with single nitrogen-vacancy (NV) centers positioned a few nanometers below the diamond surface. Such NV centers are nanoscale magnetic field detectors (18, 19) capable of detecting the magnetic field from small spin ensembles (8, 20, 21) down to the level of individual molecules (9, 22) and nuclei (23). Although the magnetic sensitivity of the NV center is sufficient for single-molecule magnetic spectroscopy to be performed, the spectral resolution is limited to $\approx 1$ kHz because of the $\approx 1$-ms spin coherence time (24). For nanoscale metrology, improving spectral resolution beyond quantum coherence limits is especially relevant because it has been shown that near-surface NV sensors have shorter coherence times and thus poorer spectral resolution (25–27). A loss of spectral resolution also occurs for high-sensitivity ensemble magnetometers as the NV density is increased (28).

For experiments, a confocal microscope with 532-nm excitation allows single, shallow NV centers to be optically detected and initialized into the $|0\rangle$ spin state (Fig. 3B). Microwaves delivered by a 20-μm copper wire provide full NV spin manipulation. Collection of fluorescence photons with an avalanche photodiode (APD) allows readout of NV spin state with a contrast of $\approx 30\%$. The arrival time of individual photons is recorded with nanosecond resolution by a time-tagged single-photon counting card and stored to computer memory, with a time stamp synchronized to a local oscillator. The same local oscillator determines the timing $T_n$ of subsequent quantum measurements, providing a timing accuracy given by the clock stability (Fig. 3A) (17).

To illustrate the frequency resolution of Qdyne, we applied an 880-nT magnetic field oscillating near 1 MHz to a shallow NV center and recorded the magnetic spectrum with both dynamical decoupling and Qdyne techniques. For dynamical decoupling, an XY8-1 sequence was used in which the spacing between $\pi$-pulses applied to the NV center was adjusted sequentially and repeated more than $10^6$ times, and the average NV fluorescence at each frequency point was recorded (8, 9, 21, 22, 25, 26). Qdyne was implemented by performing an XY8-1 measurement with a fixed delay of 500 ns between $\pi$-pulses, in which the total spin readout and reinitialization time were adjusted so that

![Fig. 1. Frequency estimation using a quantum sensor. (A) Quantum metrology with a two-level system. A spin qubit is used to measure frequency components of a time-varying Hamiltonian. The interaction period is limited by the qubit coherence time, after which the qubit state is read out. (B) Conventional quantum spectroscopy. A spectral filter is generated during the interaction period by pulsing or driving the sensing qubit. For the XY8 sequence, the filter is centered near frequency $1/2\tau$, where $\tau$ is the interpulse delay, and has a width inversely proportional to the interaction time. The filter is scanned stepwise during multiple measurements in order to acquire a complete spectrum. (C) A single interaction period at each detection frequency is repeated multiple times so as to provide a better frequency estimate. The uncertainty in frequency precision usually scales as the square root of the number of measurements.](http://science.sciencemag.org/)

![Fig. 2. Qdyne detection scheme. The output state of the sensor qubit depends on the initial phase $\phi_0$ of the signal field. The measurement result is recorded and synchronized with an external clock before the next measurement is performed for a second signal phase $\phi_2$. This procedure is repeated for the entire measurement time $T$. By heterodyning with an external clock, the NV population—and therefore the measured photon intensity—records the signal phase evolution in time. A FFT then allows the signal frequency, with respect to local oscillator (osc.) frequency, to be determined. For Qdyne detection, the precision of frequency estimation scales as $T^{-3/2}$.](http://science.sciencemag.org/)
The physical structure of the NV center is a nitrogen atom adjacent to a vacancy in the diamond lattice. (Bottom) Qdyne detection of the same magnetic field yields a spectrum with a linewidth of 607 kHz. Conventional XY8 magnetometry of a 1-MHz magnetic field, resulting in a linewidth of 300 kHz. The measured linewidth of 2 kHz is determined by the stability of the clock that is used. Although the interaction period is shorter than the coherence time of this center, the Qdyne linewidth is eight orders of magnitude narrower than achievable by using dynamical decoupling.

The measured linewidth of 2 kHz agrees with this analysis. We stress here that the local oscillator still defines measurement resolution, and the recorded linewidth is due to the physical parameters of the sample. The recorded spectrum is well replicated by performing a rigorous atomistic simulation of a 6 by 12 by 12 nm volume (Fig. 3D). The simulation modeled $7 \times 10^7$ diffusing nuclear spins interacting with the NV center, neglecting internuclear correlations but taking the effect of measurement back-action from the NV center on the nuclei into account (17).

In Fig. 4, we investigate and compare in detail the SNR, spectral linewidth, and frequency precision of Qdyne and dynamical decoupling magnetometry as a function of measurement time. Again, a stable 1-MHz source was recorded with each technique for various measurement times, and the spectra are plotted in Fig. 4A with offsets for clarity. Both spectra show raw data without smoothing, but for the dynamic decoupled (XY8-1) spectra, Lorentzian fits are included. Although the sensitivity of both techniques scales as $T_1^{-1}$, photon shot-noise limited sensitivity— it is apparent that the SNR of Qdyne is superior to that of conventional XY8 spectroscopy, with a 21-fold improvement in sensitivity (Fig. 4B). The reason for this is twofold. First, Qdyne is more sensitive to weak magnetic fields by virtue of allowing projective readout around an arbitrary axis in order to maximize readout contrast, whereas this is not generally the case for XY8 spectroscopy (Fig. 2) (17). As the magnetic field strength reduces, the sensitivity enhancement of Qdyne becomes even more pronounced. Second, the SNR of dynamical decoupling spectroscopy decreases as the number of points in the spectrum increases because less time is spent acquiring data at each frequency point. For the 50-point XY8-1 spectrum shown here, this accounts for a reduction in sensitivity by a factor of 7. Inefficient use of resources is overcome with Qdyne by means of parallel recording of all frequencies in a given bandwidth by using Fourier transform spectroscopy, resulting in a 441-fold speed-up in measurement time.

In Fig. 4C, we illustrate in more detail how the resolution gains of Qdyne are achieved. For conventional XY8 spectroscopy, the resolution is limited by the sensitivity of both techniques scales as $T_1^{-1}$, motivating work by using the NV nuclear spin as a memory to achieve few-hertz-resolution spectroscopy (17). Whereas the sensing/storage duration of dynamical decoupling and quantum memory techniques fixes the measurement resolution, for Qdyne the resolution improves linearly with measurement time, eventually saturating because of the stability of the clock that is used. Consequently, after a 1-s measurement time a 1-Hz resolution is achieved, even when temporal overheads of sensor readout and preparation are taken into account. At longer times, we observed a resolution slightly greater than $1/T_1$—for example, 2.7 MHz after 500 s—which is likely due to Allan deviation of the local oscillator.

In addition to reaching a frequency resolution orders of magnitude beyond that given by the...
sensor coherence time, the temporal scaling of the Qdyne linewidth affects the accuracy of frequency estimation. As expected, the frequency precision of XY8 spectroscopy scales close to $T^{-3/2}$, whereas the precision obtained with Qdyne scales as $T^{-3/2}$, as long as the local oscillator remains stable (Fig. 4D). A frequency precision beyond the associated linewidth is obtained by performing a least-squares fit of the spectra and plotting the estimated value (with 95% confidence intervals of fit accuracy) as a function of measurement time. Through a theoretical analysis of the frequency precision of each technique, we detail how this scaling is achieved. We follow the convention used in amplitude estimation by performing the analysis for the case of a perfect, $\delta$-frequency signal.

Two main ingredients provide the improved performance of Qdyne over dynamic decoupling and quantum memories. First, storing information from each readout onto a hard drive with practically infinite lifetime overcomes the fragility of quantum sensors and allows the signal to be reconstructed over arbitrarily long periods so that a robust clock can be used to its fullest potential. Second, Qdyne removes temporal overhead because the sensor continually samples the external field rather than storing phase information on a quantum memory and waiting before continuing with the next measurement. From a practical perspective, Qdyne also bypasses the physical overhead of hybrid quantum sensors by removing requirements for additional quantum bits and quantum gates. The precision of frequency estimation, as for amplitude estimation, depends linearly upon signal to noise, but with an additional factor because of the signal linewidth. The first (signal to noise) ingredient scales as the square root of the time, whereas the second (resolution) scales linearly with time. Combining both, a precision scaling of $T^{-3/2}$ is achieved.

The precision obtained with dynamical decoupling is given by $\Delta\nu^{DD} = \frac{kT}{ADnLO}$, where the relation can be made exact by including readout parameters. A similar result is obtained when using a memory qubit: $\Delta\nu^M = \frac{1}{ADqDD}$, where $T_M$ is the coherence time of the memory qubit (17). Here, we have assumed a best-case scenario in which each point of the spectrum samples the signal and thereby gives an equal contribution to the precision; however, this is often not the case and results in poorer precision.

For Qdyne, the combination of linewidth and sensitivity gives a precision $\Delta\nu^{Q} = \frac{1}{ADqQD}$, which is valid for measurement times up to the stability of the local oscillator. The factors $T$, $\sqrt{T}$, and $\sqrt{Tz}$ originate respectively from the regular inverse time scaling of resolution [which in previous methods was limited by the coherence time of the quantum probes (7–9, 20–23)]; the signal to noise, which improves as the square root of the number of measurements; and the rotation of the sensor by a larger angle as the interaction is prolonged. For measurement times exceeding the clock stability $T_{LO}$, the precision of Qdyne follows the standard quantum limit $\Delta\nu^Q = \frac{1}{ADqDD}$ (Fig. 4D).

A comparison between the ultimate precision limits of Qdyne and dynamical decoupling/quantum

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**Fig. 4. Performance of Qdyne (and conventional XY8) spectroscopy.** (A) Magnetic spectra recorded with Qdyne (top, 1 to 1000 s measurement times) and XY8 (bottom, 10 to 1000 s measurement times) techniques. Lorentzian fits to XY8 data are shown as dotted lines. Both techniques show photon shot-noise limited sensitivity, with SNR increasing as $\sqrt{T}$. At measurement times longer than the external clock stability of ~500 s, the SNR of Qdyne is reduced. (B) Spectral resolution of Qdyne and XY8 techniques versus measurement time. The full width at half maximum (FWHM) of the signal measured with XY8 magnetometry is set by the interaction time and remains constant at 300 kHz for the measurement duration. The resolution of Qdyne improves linearly with measurement time, including overheads of sensor readout and preparation time, until the external clock stability is reached. (D) Precision of frequency estimation for Qdyne and XY8 techniques as a function of measurement time, determined with least-squares fitting of the signal peak (supplementary materials, materials and methods and supplementary text). Whereas the precision of XY8 magnetometry improves near the standard quantum limit $T^{-1/2}$, as expected for independent measurements—Qdyne displays a precision improving as $T^{-3/2}$. (E) FFT spectroscopy of multiple fields by using Qdyne. Simultaneous detection of magnetic fields at three different frequencies (separated by 25 and 22 Hz) and generated by three independent signal generators. (F) Frequency bandwidth of Qdyne. The sensitivity to magnetic fields of different detuning is plotted in comparison with the XY8-1 filter function (green line). Each spectrum, shown with a different color, is recorded for the same amount of time. The total integrated signal for each detuning is plotted with a purple circle.
memory techniques gives $\frac{\Delta T_2}{\Delta T_2} = \frac{T_2}{T_2}$ and $\frac{\Delta T_1}{\Delta T_1} = \frac{1}{T_2}$, where all relations have been derived in the limit of a weak signal $k T_2 < 1$; that is, the sensor rotates around a small angle (this was the case for the experiments realized here). Under this condition, and given $T_{1D} > T_2, T_M$, substantial improvement in precision can be achieved with Qdync as much as nine orders of magnitude in comparison with dynamic decoupling (Fig. 4D).

The final absolute precision of 2 $\times$ 10$^{-6}$ Hz reached with Qdync here corresponds to a frequency estimation of the 1-MHz signal at the 11th fractional digit ($\Delta f/N \approx 10^{-11}$).

Because of the rigorous nature of the Heisenberg limit in quantum measurement, claims of a precision scaling beyond either $T^{-3}$ or $N^{-1}$ warrant further discussion. One may take the stance that Qdync continuously samples an oscillating field; therefore, the entire sequence should be treated as a single measurement. From this classical signal analysis perspective, the Cramer-Rao bound yields the same precision scaling as that of $\Delta f^2$ [29]. From the alternate quantum metrology framework, in which each readout of the quantum sensor constitutes a measurement, a $T^{-3/2} (or N^{-3/2})$ scaling in terms of available resources is achieved. Such a precision scaling is achieved when each measurement duration is fixed at $T_2$; the absolute precision is maximized, so that no leveraging of dynamical range occurs, as is the case for adaptive feedback schemes [30]. Further analysis of the Fisher Information gives a superlinear precision scaling, and in the case of infinitely long probe coherence time, a Heisenberg limited precision of $T^{-2}$ is obtained (supplementary material, materials and methods and supplementary text) [31–33]. As such, Qdync does not break the Heisenberg limit but takes advantage of the extra parameter space afforded to frequency measurements in quantum metrology.

In Fig. 4E, we highlight the fast Fourier transform (FFT) spectroscopy mode of Qdync, in which all spectral components in a given bandwidth are acquired simultaneously. In the context of acquiring sparse spectra, FFT spectrometers offer substantial enhancement over “frequency-swept” spectrometers because the time spent collecting no data (dead time) is removed. To demonstrate, we recorded the spectrum from three independent signal generators with 7-mHz resolution, over a measurement duration of 180 s. For the measured frequency differences of 22 and 25 Hz, $\sim$10,000 data points span the spectrum. Obtaining the same signal to noise by using conventional methods is prohibitively long, taking an estimated 500 hours [(15) for comparison].

The bandwidth of the Qdync technique can be adjusted by tuning $T_1$ because it determines the sampling rate, which sets an upper limit on the detection frequency. For the case that the sensor readout time is a small fraction of the signal accumulation time, the detection bandwidth closely approximates the filter function of the implemented XY8 sequence. In Fig. 4F, we plot a series of Qdync spectra recorded with an XY8-1 sequence centered at 1 MHz ($\tau = 500$ ns), in which the signal frequency was recorded for 100 s for a series of frequency detunings. The recorded signal amplitude follows the expected behavior given by the XY8 filter function (Fig. 4F, green), until a detuning of several kilohertz. The earlier-than-expected decay is currently not well understood but appears to be related to a relative timing instability of the external clock, leading to a broadening of the signal. Linewidth broadening reduces the precision amplitude but not the total power; by integrating the area of each curve (Fig. 4F, purple points), the expected bandwidth of the Qdync technique was recovered. There is an inherent trade-off between magnetic sensitivity and bandwidth because magnetic sensitivity can be increased by extending each interaction period $T_2$ (up to a maximum value of $T_2$), but this comes with a commensurate reduction in bandwidth. Likewise, the sensitivity can be increased by spending more time reading out the sensor, again with a decrease in bandwidth owing to a lower sampling rate.

Our spectroscopic technique, which references a sensitive qubit to a stable oscillator, allows a resolution beyond the $T_2$ limit of the quantum sensor to be reached and surpasses the standard quantum limit for identical and independent measurements to achieve a $T^{-3/2}$ frequency precision scaling. By applying Qdync to shallow NV centers in diamond, we achieved an increase in frequency precision and resolution by nine and eight orders of magnitude, respectively, over dynamic decoupling. The application of Qdync to nonscale NMR spectroscopy, in which gains in frequency precision translate to spatial resolution, has implications for molecular structural determination. Last, the low technical demands of Qdync, which bypasses the need for hybrid quantum systems, make the technique widely applicable for high-resolution magnetic spectroscopy.

REFERENCES AND NOTES

17. Materials and methods are available as supplementary materials.
32. S. P. Jing Yang, A. N. Jordan, Quantum parameter estimation with the Landau-Zener transition, arxiv:1612.02390 (7 December 2016).

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Enhancing quantum sensing

The quantum properties of the nitrogen vacancy (NV) defect in diamond can be used as an atomic compass needle that is sensitive to tiny variations in magnetic field. Schmitt et al. and Boss et al. successfully enhanced this sensitivity by several orders of magnitude (see the Perspective by Jordan). They applied a sequence of pulses to the NV center, the timing of which was set by and compared with a highly stable oscillator. This allowed them to measure the frequency of an oscillating magnetic field (megahertz bandwidth) with submillihertz resolution. Such enhanced precision measurement could be applied, for example, to improve nuclear magnetic resonance-based imaging protocols of single molecules.

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