Determination of the position of a single nuclear spin from free nuclear precessions detected by a solid-state quantum sensor

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(Received 31 May 2018; published 13 September 2018)

We report on a nanoscale quantum sensing protocol which tracks a free precession of a single nuclear spin and is capable of estimating an azimuthal angle—a parameter which standard multipulse protocols cannot determine—of the target nucleus. Our protocol combines pulsed dynamic nuclear polarization, a phase-controlled radio-frequency pulse, and a multipulse ac sensing sequence with a modified readout pulse. Using a single nitrogen-vacancy center as a solid-state quantum sensor, we experimentally demonstrate this protocol on a single $^{13}$C nuclear spin in diamond and uniquely determine the lattice site of the target nucleus. Our result paves the way for magnetic resonance imaging at the single-molecular level.

DOI: 10.1103/PhysRevB.98.121405

Nuclear magnetic resonance (NMR) spectroscopy is an analytical technique extensively used in chemistry, biology, and medicine. It achieves sub-ppm spectral resolutions to provide a wealth of information on the structure and chemical environment of molecules, but requires at least nanoliter-volume analytes containing an ensemble of identical nuclei, due to the insensitive induction detection the technique relies on. In recent years, single isolated electron spins in solids, most prominently those associated with nitrogen-vacancy (NV) centers in diamond [1–3], have emerged as atomic-scale quantum sensors capable of detecting weakly coupled external nuclei in as small as zeptoliter volumes, a dramatic decrease compared with conventional NMR [4–6]. Furthermore, various NMR protocols, in which a train of properly timed microwave pulses interrogates precessing nuclear spins via the interaction with the sensor electron spin, have been devised and applied to external nuclei, demonstrating identifications of isotopes [7–9], detection of single protons [10], spectroscopy of single proteins [11], spectral resolution approaching that of conventional NMR [4–6].

For nuclei dipolarly coupled with a sensor, the knowledge of the hyperfine parameters $A_r$ and $A_\perp$ (the parallel and perpendicular components, respectively) translates to the coordinate parameters $r$ and $\theta$, the distance from the sensor and the tilt (polar angle) from the applied static magnetic field $B_x$, respectively, owing to the form of the interaction $\propto(3\cos^2\theta - 1)/r^3$ or $3\cos\theta \sin\theta/r^3$ [Fig. 1(a), left]. $^{13}$C nuclei ($I = \frac{1}{2}$) in diamond sensed by the NV electronic spin ($S = 1$) have served as a canonical testbed for various NMR protocols to characterize the hyperfine parameters [3,18–25]. For instance, in correlation spectroscopy, a multipulse sequence is repeated with the interval of $t_{\text{corr}}$, during which a target nuclear spin evolves freely. Boss et al. demonstrated that, by engineering the Hamiltonian during the free nuclear precession, both $A_r$ and $A_\perp$ can be estimated with high precision [24]. The information that is still missing in order to uniquely determine the position of a target nuclear spin is the azimuthal angle $\phi$ [26–28], which, due to the symmetry of the interaction, does not formally appear in the Hamiltonian.

In this Rapid Communication, we show that the azimuthal angle can be determined by a multipulse protocol combined with dynamic nuclear polarization (DNP) and radio-frequency (rf) control of a target spin. As a proof of principle, we apply this protocol to the NV-$^{13}$C -coupled system, and uniquely assign the lattice site that the $^{13}$C nucleus sits in, even when multiple sites equivalent to it exist.

Our protocol proceeds as follows [see Figs. 1(b)–1(g) for the pulse sequences used]. The target nuclear spin is first polarized by transferring the polarization of the sensor electron spin using a multipulse sequence called PulsePol [29], and is tipped to the $xy$ plane by an rf $\pi/2$ pulse. The dipolar field experienced by this tipped nuclear spin is dependent on $\phi$; an example to appreciate this is that, when two nuclear spins are located on opposite sides of the sensor, the directions of the dipolar fields are opposite [Fig. 1(a), middle]. A subsequent free precession of each nuclear spin carries this information as the initial phase of the oscillation [Fig. 1(a), right].

A central issue that must be addressed in this scenario is how to detect the phase of a nuclear precession. Here, we consider a particular example in which $|m_S = 0\rangle$ and $|m_S = -1\rangle$ sublevels of the NV spin serve respectively as $|0\rangle$ and $|1\rangle$ of the sensor two-level system, but the concept is general. To detect a dynamics of a single nuclear spin, the sensor spin is prepared in a superposition of $|m_S = 0\rangle$ and $|m_S = -1\rangle$, and is subject to a Carr-Purcell (CP) sequence [30] consisting of $N\pi$ pulses equally separated by $\tau$ [Fig. 1(b)]. Because only

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When $|n_S = -1\rangle$ can hyperfine couple with the nuclear spin, the two sensor states act differently on the nuclear spin, making it rotate around different axes, say, $n_0$ and $n_1$. Different nuclear dynamics are combined by the final $(\pi/2)_X$ pulse $(\pi/2$ pulse with the X phase defined in the rotating frame of reference). The transition probability $P_X$ of the sensor is given by [21]

$$P_X = 1 - \frac{1}{2}(1 - n_0 \cdot n_1) \sin^2 \frac{N\phi_{cp}}{2}. \quad (1)$$

When $\tau$ is chosen properly, $\phi_{cp}$ and $n_0 \cdot n_1$ carry the information on a single nuclear spin. This readout pulse has been extensively used to probe the nuclear dynamics in the past [21,31], but does not depend on the free precession angle of the nuclear spin.

In our protocol, we instead use a $(\pi/2)_{\gamma}$ pulse for the readout. The transition probability becomes

$$P_{\gamma} = \frac{1}{2} - \frac{1}{2} \cos(\phi - \phi_0) \sin N\phi_{cp}, \quad (2)$$

where $\phi_0$ is the azimuthal angle of the nuclear spin measured in real space. A detailed deviation of Eq. (2) is given in the Supplemental Material [32]. We measure a free precession of a nuclear spin, which oscillates as $\cos(2\pi f_{cp}t + \phi_0)$. $\phi$ is determined as $\phi = \phi_0(0) + \phi_0, \phi_0(0)$ is the azimuthal angle of the nuclear spin at $t = 0$ [defined as the end time of an rf pulse, Fig. 1(g)]. While to our knowledge Eq. (2) has not been explicitly given in previous literature, a recent demonstration of high-resolution spectroscopy of nuclear spin ensembles does employ this $(\pi/2)_{\gamma}$ readout [13]. There, an oscillating collective magnetization induced by an rf pulse is phase coherent, and a free nuclear precession analogous to a free induction decay in conventional NMR has been recorded (called the coherently averaged synchronized readout). It should be noted that, for a single unpolarized nuclear spin, random nuclear orientations average out nuclear precession signals. We detect a freely precessing single nuclear spin by polarizing it, and in this case the signal is coherently averaged to reveal its oscillation phase.

Experiments were performed using a type-IIa (001) diamond substrate from Element Six. Single negatively charged NV centers in bulk ($\sim 50 \mu m$ deep) are optically resolved by a home-built confocal microscope equipped with a 515-nm excitation laser for the initialization and readout of the NV spin. The fluorescence from a single NV center is collected by a single-photon counting module, and the microwave to manipulate the NV spin is delivered through a copper wire running across the diamond surface. The rf signal to control the NV spin is delivered through a copper wire bonded on the back side of the sample mount. This configuration makes the magnetic field from the coil roughly point normal to the sample surface, but the deviation from it is carefully calibrated [32]. We select an NV center with its symmetry axis along the [111] crystallographic direction, and $B_0$ of 36.2 mT is applied along the same direction.

We first characterize the magnetic environment of this NV sensor. The primary purpose here is to find a single $^{13}$C nucleus whose coordinate parameters $\tau$ and $\theta$ are known so that our protocol may be applied to determine $\phi$ and thus its exact position (lattice site). We apply the CP sequence, in which $\tau$ is incremented with $N$ fixed as 16, and obtain the spectrum shown in Fig. 2(a). The broad dip observed around the bare $^{13}$C Larmor frequency $f_\text{c}$ is $\gamma^c B_0 = 387.5 kHz$ originates from weakly coupled bath $^{13}$C nuclei, whereas the sharp dip at $f_\text{c} = 301.6 kHz$ is indicative of a single $^{13}$C nucleus strongly coupled to the sensor. The latter signal is examined in more detail by incrementing $N$ of the CP sequence with $\tau$ fixed at a near-resonance condition of 1.6875 $\mu s = 1/(2 \times 296 kHz)$ [Fig. 2(b)]. The $^{13}$C nuclear spin then nutates approximately about the $A_1$ axis. For sufficiently large $N$, it makes coherent, full $2\pi$ rotations multiple times at the frequency $f_{cp}$ of 10.2 kHz. Simulations also confirm that we
are observing a single nuclear spin and not multiple nuclear spins with the same hyperfine parameters [32].

We further analyze this $^{13}$C nucleus by correlation spectroscopy [Fig. 1(e)]. Figure 2(c) shows a modulated oscillation as increasing $t_{\text{corr}}$, and its Fourier transformation reveals two peaks at $f_0 = 387.5$ kHz and $f_1 = 215.6$ kHz. $f_0$ corresponds exactly to $f_c$, and therefore results from the coupling with $|m_S = 0\rangle$. On the other hand, $|m_S = -1\rangle$ exerts the hyperfine field on the nuclear spin, shifting its precession frequency. The target nuclear spin is properly probed because $(f_0 + f_1)/2 = 301.55$ kHz $= f_c$, and the negative shift $(f_1 - f_0 < 0)$ suggests negative $A_\parallel$. Combining these results, we deduce $A_\parallel = -173.1$ kHz and $A_\perp = 22.3$ kHz with an accuracy of about 0.1 kHz [32].

It should be noted that, unlike the case of external nuclear spins, $A_\parallel$ and $A_\perp$ estimated here are not purely dipolar in nature due to the presence of a relatively strong contact hyperfine interaction. This usually complicates the direct estimation of the coordinate parameters $r$ and $\theta$ from $A_\parallel$ and $A_\perp$. However, the estimated values are accurate enough to be compared with theoretical calculations. Nizovtsev et al. have recently performed an extensive density functional theory (DFT) simulation of a C$_{510}$[NV]H$_{252}$ cluster [33]. From their list of hyperfine parameters for 510 carbon sites, we find that six sites labeled as C218, C226, C230, C240, C280, and C282 show close agreement with the experimental values. The hyperfine parameters of these sites are, in kHz units, $(A_\parallel, A_\perp) = (-175.4, 21.7), (-176.7, 21.7), (-174.7, 21.7), (-177.1, 21.9), (-173, 22),$ and $(-173.4, 22.1)$, respectively [average: $(-175.1 \pm 2.1, 21.9 \pm 0.2)$]. The positions of these candidate sites are given in Fig. 2(d). In all cases, we obtain $r = 6.84$ Å and $\theta = 94.8^\circ$ [32].

The next task is to polarize the target nuclear spin. For this, we use a pulsed technique called PulsePol, which is yet another application of Hamiltonian engineering [29]. Figure 1(d) shows two PulsePol sequences labeled as PolY and PolX. One cycle consists of eight pulses with a total duration of $2T_{\text{pol}}$. When $2T_{\text{pol}} = k/f_0$ is satisfied ($k$: odd integer; $f_0$: nuclear Larmor frequency), the average Hamiltonian of a hyperfine-coupled electron-nuclear system becomes proportional to $S_z I_z + S_+ I_-$ (flip-flip) or $S_z I_z + S_- I_+$ (flip-flip), driving the polarization transfer between the electron and the nuclei. It is shown that for $k = 3$ PolY (PolX) drives flip-flip (flip-flip), whereas for $k = 5$ PolY (PolX) does flip-flip (flip-flip) [32]. Because the NV spin is optically initialized into $m_S = 0$, PolY (PolX) for $k = 3$ polarizes the nuclei into $m_I = -\frac{1}{2}$ ($\frac{1}{2}$). For $k = 5$, the direction of the nuclear polarization becomes opposite.

We test the performance of PulsePol by successive application of PolX and PolY, as shown in Fig. 1(e). The first PolX serves to depolarize the nuclear polarization during a previous run, and the polarization transfer by PolY is read out as a decrease of the $m_S = 0$ polarization ($P_0$) [34]. The circle $(\circ)$ points in Fig. 3 are the result of this measurement with $N_{\text{pol}} = 5$. Two “replicas” of the NMR spectrum in Fig. 2(a) are clearly observed at $\frac{5}{3}$ and $\frac{7}{3}$ of the NMR conditions, as expected. Furthermore, a single nuclear spin can be selectively polarized by applying the sequence of Fig. 1(f). This sequence works as follows: (1) PolY is executed nine times in order to fully polarize the nuclei. (2) A microwave $\pi$ pulse drives the NV spin into $m_S = -1$. (3) An rf $\pi$ pulse tuned at $f_1 = 215.6$ kHz is applied. The NV spin being $m_S = -1$, only the
...target nuclear spin is resonantly flipped by this rf pulse. (4) By the final PolY, the polarization transfer acts only on the flipped nuclear spin, as other nuclei have already been polarized. The square (□) points in Fig. 3 clearly demonstrate the power of selective polarization; dips are observed only at $f_1/3$ and $f_1/5$, with all other dips almost completely disappeared.

We now demonstrate the protocol of Fig. 1(g) to determine $φ$. Either PolY or PolX is applied with $N_{pol} = 5$, $N_{rep} = 5$, and $τ_{pol} = 4.9760 \, \mu s$. $τ_{pol}$ satisfies $3/(2τ_{pol}) = f_1$, for which PolY (PolX) polarizes the target nuclear spin into $m_I = -\frac{1}{2}$ ($\frac{1}{2}$). A phase-controlled selective rf $π/2$ pulse tuned at $f_1$ is applied, followed by the CP sequence with the $(π/2)Y$ readout ($N = 16$, $τ = 1.6608 \, \mu s$). The rf pulse length is chosen to be 102.041 $μs$, matched with 22 oscillation periods (22/$f_1$), in order to suppress unwanted phase acquisitions by the rf field along the $z$ axis [32]. Figure 4(a) shows an exemplary trace as changing $t$. Here, PolY is used, and the waveform of the rf signal is a sine wave, for which we define the rf phase $φ_{f_1} = 270°$. The data are fitted by $A \cos(2πf_1t + φ_0) + B$ (red curve). $f_1$ agrees well with $f_1$, confirming that the free precession of the target nuclear spin is indeed detected.

We note that the minimum $t$ is set as $t_0 = 6.872 \, \mu s$ in order to avoid an overlap with an rf pulse, whereas our aim here is to estimate the oscillation phase at $t = 0$. To accurately estimate $φ_0$ under this constraint, oscillations should be taken as long as possible. This requires a dauntingly long measurement time, and at the same time exceedingly high stability of the experimental setup. We therefore choose to undersample the data points for further measurements; by taking less points, $t$ is instead increased up to 1 ms ($<T_1 \approx 5 \, ms$), and yet the original $φ_0$ is recovered by appropriately setting the measurement parameters [32]. Figure 4(b) shows $φ_0$ determined in this way. The linear dependence on $φ_{rf}$ is observed, as expected [32]. $φ_0$ is $180°$ shifted between PolY and PolX, confirming that the two sequences polarize the nuclear spin into opposite directions. From the fit, we obtain $φ_0 = φ_f + 334.0° \pmod{360°}$. On the other hand, if we take into account the azimuthal angle of the rf field in this coordinate and the effect of detuning ($f_0 − f_1$), we can estimate $φ_0$ as $−φ_{rf} + 89.2°$ [32]. Together, we obtain $φ$ as 243.2 ± 5.3° [dashed line in Fig. 4(b)], $φ_0(0)$ can be estimated more accurately by simulating the dynamics of the nuclear spin [32]. The simulations give $φ = 248.8 ± 2.7°$ (dotted line) or $247.8 ± 4.1°$ (solid line), marginally dependent on the parameters used. Figure 4(c) shows the accuracy ranges of $φ$ determined by these estimations, and there is at most one lattice site that falls on this range; we have been able to pinpoint the lattice site of the target nuclear spin [32].

To summarize, we have described a protocol which tracks a free precession of a single nuclear spin. Combined with DNP and a phase-controlled rf pulse, our method is capable of determining the azimuthal angle of the target nuclear spin. A particular experimental demonstration was performed on a single $^{13}$C nuclear spin and its lattice position was uniquely pinpointed. Previously, the position of a single $^{13}$C nuclear spin in diamond had been estimated by analyzing NMR spectra taken at three differently oriented $B_0$ [22]. When the NV center or other solid-state defects with $S > \frac{1}{2}$ electron spin is used as a sensor, an application of $B_0$ misaligned from the sensor quantization axis complicates the analysis. The present protocol circumvents this issue. Looking ahead, we imagine that the present protocol could be employed for three-dimensional mapping of nuclear spins in a single molecule positioned on a near-surface NV sensor [35]. The nuclear-nuclear interactions within the immobilized molecule can be suppressed using dipolar decoupling sequences such as WAHUHA and MREV [12,36], which are compatible with our protocol. The protocol can also be combined with the high-resolution spectroscopy method [13,37,38], so that chemical shifts and $J$ couplings could be resolved. Thus, our result paves the way for magnetic resonance imaging at the single-molecular level.

Note added. Recently, we became aware of an article by Zopes et al., which reported a similar method to locate single nuclear spins [39].

The authors thank C. L. Degen, J. Zopes, and J. Boss for helpful discussions, especially on the preparation and calibration of an rf coil, and also for letting us know about their related work [40]. K.S. is supported by JSPS Grant-in-Aid for Research Fellowship for Young Scientists (DC1) No. JP17J05890. K.M.I. is supported by JSPS Grant-in-Aid for Scientific Research (KAKENHI) (S) No. 26220602, JST Development of Systems and Technologies for Advanced Measurement and Analysis (SENTAN), JSPS Core-to-Core Program, and Spintronics Research Network of Japan (Spin-RNJ).
Determination of the position of a single nuclear ... Physical Review B 98, 121405(R) (2018)


