Spurious harmonic response of multipulse quantum sensing sequences

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Multipulse sequences based on Carr-Purcell decoupling are frequently used for narrow-band signal detection in single spin magnetometry. We have analyzed the behavior of multipulse sensing sequences under real-world conditions, including finite pulse durations and the presence of detunings. We find that these non-idealities introduce harmonics to the filter function, allowing additional frequencies to pass the filter. In particular, we find that the XY family of sequences can generate signals at the $2f_{ac}$, $4f_{ac}$, and $8f_{ac}$ harmonics and their odd subharmonics, where $f_{ac}$ is the ac signal frequency. Consideration of the harmonic response is especially important for diamond-based nuclear spin sensing where the NMR frequency is used to identify the nuclear spin species, as it leads to ambiguities when several isotopes are present.

I. INTRODUCTION

Multipulse decoupling sequences, initially developed in the field of nuclear magnetic resonance (NMR) spectroscopy [1, 2], have enjoyed a renaissance for the control of individual quantum systems [3–6]. The concept relies on periodic reversals of the coherent evolution of the system, where the effect of the environment is canceled over the complete sequence. Multipulse decoupling can be regarded as an efficient high-pass filter that averages out low frequency noise.

It has recently been recognized that decoupling sequences with equal pulse spacing offer an opportunity for sensitive ac signal detection [7]. By tuning the interpulse delay $\tau$, the sequence can be made commensurate with a signal’s periodicity leading to recoupling – that is, the decoupling fails for a specific set of signal frequencies that are an odd multiple of $1/(2\tau)$ (see Fig. 1a). The quantum system then effectively acts as a narrow-band lock-in amplifier [8] with demodulation frequency $f = k/(2\tau)$ and approximate bandwidth $f/(N/2)$, where $N$ is the total number of pulses in the sequence and $k = 1, 3, 5, \ldots$ is the resonance order. A precise transfer function of decoupling filters has been given in several recent papers [7–9].

Multipulse sensing can greatly improve detection sensitivity, as it selectively measures the influence of a desired ac signal while suppressing unwanted noise. Moreover, the technique presents an opportunity to perform spectroscopy over a wide frequency range [9–12]. A particularly important application has been the detection of nanoscale NMR signals using single spins in diamond where the nuclear Larmor frequency is taken as a fingerprint for the detected spin species [13–21]. Although mostly developed in the context of single spin magnetometry, multipulse sensing sequences have been applied to other quantum systems including trapped ions [8] and superconducting qubits [10, 11].

In this paper we consider a specific class of multipulse sensing sequences known as the XY-family of sequences [22]. XY-type sequences use the common template of equidistant $\pi$ pulses, but pulse phases are judiciously alternated so as to cancel out pulse imperfections, such as pulse amplitude or detuning. The XY-family has become widely popular for measurements that require a large number of pulses $N$, and it has been the sequence of choice for most reported NV-based NMR experiments [16–21].

Here we show that the phase alternation of XY-type sequences causes additional frequencies to pass the multipulse filter. In particular, we show that an ac signal with frequency $f_{ac}$ will produce response at the $2^{\text{nd}}$, $4^{\text{th}}$ and $8^{\text{th}}$ harmonics (and their $k^{\text{th}}$ subharmonics), depending on the sequence used. The harmonics are caused by a combination of time evolution during the finite duration of $\pi$ pulses and the “superperiods” introduced by phase cycling. Although the feature is generic to all experiments, it is most prominent for low pulse amplitudes, short interpulse delays, and if a static detuning is present. The feature is significant because it leads to further ambiguities in signal analysis and complicates interpretation of spectra.

II. THEORY

In order to understand the generation of harmonics we consider the simple case of an XY4 sequence exposed to an ac signal with frequency $f_{ac}$. The basic building block of the XY4 sequence consists of four $\pi$ pulses with alternating $X,Y$ phases [22] (see Fig. 1b,c). In an ordinary sensing experiment, the interpulse spacing $\tau$ is matched to half the periodicity of the ac signal ($f = f_{ac}$), leading to a constructive addition of phase during free evolution intervals. The phase accumulated per period $\tau$ is

$$\phi_{\text{free}} = \frac{2\Omega \tau}{\pi},$$  \hspace{1cm} (1)$$

and the phase accumulated during the entire sequence is $N\phi_{\text{free}}$, where $\Omega$ is the amplitude of the ac signal. $\Omega$ represents a coupling constant with units of angular frequency.
This corresponds to a net rotation around the y-axis by an angle $4\theta_{\text{eff}} \approx 4\Omega/\omega_1$. The sensor therefore acquires an additional “anomalous” phase during the XY4 block, on average

$$\phi_\pi \approx \theta_{\text{eff}} \approx \frac{\Omega t_\pi}{\omega_1}$$

(4) per $\pi$-pulse, where $t_\pi$ is duration of the square-shaped pulse. A similar calculation can be made for XY8 and XY16 sequences and for other harmonics, and resulting phases have been collected in Table I.

The anomalous phase $\phi_\pi$ can be compared to the ordinary phase $\theta_{\text{free}}$, providing a “relative strength” $r = \phi_\pi/\theta_{\text{free}}$ of harmonics compared to the fundamental signal. For the example of the 2nd harmonic in XY4 detection,

$$r = \frac{\phi_\pi}{\theta_{\text{free}}} = \frac{t_\pi}{2\pi}.$$  (5)

Other harmonics and sequences follow by using the appropriate multiplier from Table I. We find that the phase accumulated during $\pi$ rotations is equal to the phase accumulated during free evolution, scaled by $t_\pi/2\pi$. Since most often $t_\pi \ll \tau$, the harmonics will typically be much weaker than the fundamental signal at $f_{ac}$. The harmonics may, however, become relevant if one intends to detect a weak ac signal in the presence of a strong, undesired signal. Note finally that higher order resonances ($k > 1$) are not attenuated (sometimes enhanced) for anomalous signals, unlike the ordinary signals where $\theta_{\text{free}} \propto 1/k$ (Ref. [13]).

### III. SINGLE-SPIN MAGNETOMETRY

The above considerations apply to several relevant situations in single spin magnetometry of nanoscale NMR signals. Here, the precessing nuclear magnetization from single nuclei [13–15] or nuclear ensembles [16–21] provides the ac signal. In the following we focus our attention on the specific case of an electron-nuclear two-spin interaction...
FIG. 2: Simulated spectra showing response as a function of detection frequency \( f = 1/(2\pi) \) for coupling to a single nuclear spin with \( f_{ac} = \omega_0/(2\pi) = 2 \text{MHz} \) and \( \Omega = a_{\perp}/2 = 2\pi \cdot 200 \text{kHz} \). (a) Ideal sensing sequence with infinitely short \( \pi \) pulses. Only the expected peaks at \( f_{ac}/k \) are observed. (b-d) XY sequences. Additional peaks at \( 2f_{ac}/k, 4f_{ac}/k \) and \( 8f_{ac}/k \) are observed, leading to a dense “forest” of peaks. Further simulation parameters were \( N = 480, \omega_1/2\pi = 20 \text{MHz} \) and (for c,d) \( \Delta_x = 1 \text{MHz} \).

system, where the electronic spin serves as the quantum sensor. The Hamiltonian of this system in a rotating frame of reference is

\[
\hat{H} = \Delta_z \hat{S}_z + \omega_1 \left( x_{mod}(t) \hat{S}_x + y_{mod}(t) \hat{S}_y \right) + a_{\perp} \hat{S}_z I_x + \omega_0 \hat{I}_z
\]

where we have grouped terms into static, control and ac contributions. \( \Delta_z \) represents a static detuning of the electron spin \( \hat{S} \) with respect to the rotating frame of reference, \( x_{mod}(t) \) and \( y_{mod}(t) \) represent the amplitude modulation of the multipulse decoupling sequence (with values between -1 and 1), \( a_{\perp} \) represents the transverse coupling to the nuclear spin \( \hat{I} \), and \( \omega_0 = \gamma_\text{n} B + a_{||}/2 \) is the Larmor frequency of the nuclear spin composed of static bias field \( B \) and parallel hyperfine field contribution \( a_{||} \) [13, 23]. \( \gamma_\text{n} \) is the nuclear gyromagnetic ratio.

Returning to our generic expression for anomalous phase accumulation, Eq. (4), we can associate \( \Omega \rightarrow a_{\perp}/2 \) and \( f_{ac} \rightarrow \omega_0/(2\pi) \). For the case of a large nuclear spin ensemble with rms nuclear field \( B_{\text{rms}} \), one would associate \( \Omega \rightarrow \gamma_\text{e} B_{\text{rms}}/2 \), where \( \gamma_\text{e} \) is the electron gyromagnetic ratio.

IV. SIMULATIONS

We have performed a set of numerical simulations [23] to investigate the time evolution of the Hamiltonian, Eq. (6). Our quantity of interest was the probability that the spin state at the end of the sequence \( |\alpha\rangle \) deviated from its original state \( |0\rangle \), expressed by the transition probability \( p = |\langle \alpha |0 \rangle|^2 \).

Fig. 2 presents simulated spectra for different multipulse sensing sequences. The top panel shows the filter response for ideal \( \pi \) rotations of infinitely short duration. As expected, signal peaks are generated at frequencies \( f = f_{ac}/k \), where \( k = 1, 3, 5, \ldots \). Lower panels, by contrast, show the filter response of XY sequences for real \( \pi \) rotations that have a finite duration. Many extra peaks appear corresponding to \( 2^{\text{nd}}, 4^{\text{th}} \) and \( 8^{\text{th}} \) harmonics of \( f_{ac}/k \). The spectra in Fig. 2 represent the response to a single ac signal (single spin) with frequency \( f_{ac} \). Obviously, if two or more signals were present, analysis of spectra would quickly become intractable.

Fig. 3 investigates the influence of a static detuning \( \Delta_z \). Several effects may be noticed. First, a static detuning exacerbates the harmonic peaks – stronger anomalous response is generated for the same ac signal magnitude \( \Omega \). Second, although not evident from this plot, peaks appear even at those harmonics where \( \Omega = 0 \) in Table I. Third, the time evolution of \( p \) becomes markedly different – values oscillate between \( p = 0 \ldots 0.5 \) in the absence of a detuning, whereas they can oscillate between \( p = 0 \ldots 1 \) and become aperiodic in the presence of a detuning.

V. EXPERIMENTS

We have experimentally verified the existence of harmonics using the nitrogen-vacancy (NV) center in diamond as the single spin sensor. The NV center is a prototype electron spin system (\( S = 1 \)) that can be optically detected at room temperature [24] and that has served as a testbed for many recent multipulse sensing experiments. For our measurements, the NV center was polarized and read out using non-resonant green laser excitation, and manipulated using microwave control pulses with adjustable phase and amplitude [17]. A static bias field was applied to lift the spin degeneracy and all sensing experiments were carried out on the \( m_S = 0 \leftrightarrow m_S = -1 \) subsystem.
In a first experiment we have recorded the XY8 response of an NV center with two proximal \(^{13}\)C nuclei \((I = 1/2)\) in a bias field of 183 mT. The nuclear Larmor frequencies of the two \(^{13}\)C nuclei in this field were \(f_{ac} = 1.97\) MHz and \(f'_{ac} = 2.08\) MHz. (The frequencies were slightly different due to a small parallel hyperfine contribution.) Fig. 4 shows the spectral response over the frequency range of \(f = 1.5 \sim 9\) MHz. We found that almost all harmonics in that range could be resolved and matched with simulations using a single set of parameters.

Fig. 5 shows a second example where the NV center’s electron spin was coupled to its own \(^{14}\)N nucleus \((I = 1)\). The \(^{14}\)N has two nuclear spin transitions, resulting in two signals with frequencies \(f_{ac} = 4.4\) MHz and \(f'_{ac} = 5.4\) MHz. Again, most expected harmonics could be observed and matched with simulations.

VI. AMBIGUITIES BETWEEN NMR SIGNALS

The feature of harmonics is of particular significance for recent nanoscale NMR experiments with near-surface NV centers. These experiments used spectral identification to discriminate different nuclear isotopes in samples by their NMR frequencies, most prominently \(^1\)H, \(^{13}\)C, \(^{19}\)F, \(^{29}\)Si and \(^{31}\)P \([16–21]\). In a recent study we found very shallow (< 3 nm) NV centers to produce signals displaying all the characteristics of single proton spins, including the Zeeman effect and a quantum-coherent coupling between sensor and target spins \([23]\).

We now show that single \(^{13}\)C nuclei can generate signatures virtually identical to those of single \(^1\)H, challenging our previous interpretation of these signals as single proton observations. We begin with the scaling of the peak frequency with magnetic field \(B\), as shown in Fig. 6.

![Fig. 6: Frequency of peak response for various magnetic bias fields \(B\). Points are measured peak positions. Solid lines have slopes chosen to be 1×, 2× and 4× the gyromagnetic ratio of \(^{13}\)C. The red dashed line has slope given by the gyromagnetic ratio of \(^1\)H, and is almost identical to the \(^{13}\)C 4th harmonic line (black line).](image)

![Fig. 5: Spectrum recorded by an NV center coupled to its own \(^{14}\)N nucleus, measured using an XY8 sequence. Common coupling constant was \(a_{\perp}/2\pi = 280\) kHz. This coupling was due to a deliberate misalignment of the bias field of ∼ 8° with respect to the NV symmetry axis. Further experimental parameters were similar to Fig. 4.](image)
in Fig. 6. The measured peak positions (points) can all be associated with the response from a single $^{13}$C nucleus at either its fundamental Larmor frequency, or its 2nd or 4th harmonic. The linear slope of the fundamental frequency (blue line) is given by the gyromagnetic ratio of $^{13}$C ($\gamma_n = 10.71 \text{MHz/T}$) and is indicative of the nuclear species, while the slopes of the two harmonic frequencies are enhanced with apparent gyromagnetic ratios of $2\gamma_n$ and $4\gamma_n$. Since the value of $4\gamma_n = 42.82 \text{MHz/T}$ coincides with the gyromagnetic ratio of protons ($\gamma_n = 42.57 \text{MHz/T}$) to within 0.6%, the nuclear isotope cannot be uniquely identified.

We found also the time evolution of fundamental and harmonic signals to produce indistinguishable signatures. Fig. 7 shows the peak of an apparent proton signal as a function of total evolution time $T = N\tau$. The oscillating signal can be reproduced by either of two simulations, one assuming the presence of a single $^1$H and one of a single $^{13}$C. Again, no conclusion can be made on the identity of the nuclear species.

The above examples illustrate that identification of signals based on a single peak is in general insufficient. A more trustworthy identification could be obtained by measuring a wider spectrum containing several harmonics. For the specific situation of $^{13}$C and $^1$H, the second harmonic at twice the $^{13}$C Larmor frequency (roughly half the $^1$H frequency) could serve as a tell-tale signature of $^{13}$C. This peak is absent for $^1$H (see Fig. 4b).

Although the ambiguity between $^{13}$C and $^1$H may be the most relevant for diamond-based NMR detection, we note that other pairs of nuclear species exists that could produce similar coincidental overlap. Potential candidates include $^1$H (1/5 harmonic) and $^{29}$Si, $^{13}$C (4/5 harmonic) and $^{29}$Si, or $^1$H (2/5 harmonic) and $^{31}$P.

VII. SUMMARY

In summary, we have investigated the spectral filtering characteristics of an important class of multipulse quantum sensing sequences, the XY-family of sequences. We found the time evolution during finite $\pi$ pulses, which is present in any experimental implementation, to cause phase build-up at higher harmonics of the signal frequency, leading to sets of additional peaks in the spectrum. We have further investigated this feature by simulations and experiments of single NV centers in diamond. The feature has particular significance for nanoscale NMR experiments that rely on spectral identification. Specifically, we found that signal detection at a single frequency is in general insufficient to uniquely assign a certain nuclear spin species.

We finally mention several sensing schemes that do not suffer from the ambiguities inherent to multipulse sequences. Namely these include rotating-frame spectroscopy [25–27] and free precession techniques [28–30]. Moreover, it may be possible to craft varieties of sequences that avoid harmonic resonances yet maintain superior static error compensation, such as CPMG-sequences with composite $\pi$ pulses [4] or aperiodic XY-sequences. Although the alternative schemes have their own restrictions and may not always be available, they could offer independent verification of spectral features.

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