Shaped Pulses for Energy Efficient High-Field NMR at the Nanoscale

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The realisation of optically detected magnetic resonance via nitrogen vacancy centers in diamond faces challenges at high magnetic fields which include growing energy consumption of control pulses as well as decreasing sensitivities. Here we address these challenges with the design of shaped pulses in microwave control sequences that achieve orders magnitude reductions in energy consumption and concomitant increases in sensitivity when compared to standard top-hat microwave pulses. The method proposed here is general and can be applied to any quantum sensor subjected to pulsed control sequences.

Introduction — Nuclear magnetic resonance (NMR) techniques applied to macroscopic samples have enabled fundamental scientific breakthroughs in organic chemistry, biology, medicine and material science, and continues to drive scientific and technological progress [2, 3]. Recently, NMR detection has been extended to the micron and nanoscale [4–6] where macroscopic detecting coils [7] are replaced by a quantum sensor based on the nitrogen-vacancy (NV) center in diamond [8–10]. These minute detectors can be located very close to the sample under study thus opening the door for the detection of NMR signals emitted by nanoscale samples or even by individual proteins or nuclei [11–16]. NV centers are particularly well suited for this purpose because their magnetic sub-levels can be initialised and read-out with laser pulses, on the NV quantum sensor to average out environmental noise while preserving the sensitivity for external signals.

Typically sensing experiments based on NV centers are performed at relatively low static magnetic fields, on the order (or lower) than a few hundred of Gauss [11, 13, 16, 19, 27], with singular exceptions as, for example, [14] and [28] that operate at thousands of Gauss. For the purposes of nanoscale NMR the realisation of detection under larger magnetic fields (on the order of several Tesla) presents a number of potential advantages. These include longer nuclear $T_1$-times [29], increased thermal spin polarisation which leads to enhanced NMR signal strength, as well as larger chemical shifts. Note that the latter are key quantities in molecular structure determination, which scale linearly with the applied magnetic field [7]. However, the application of large magnetic fields also poses significant challenges caused by the increase of the nuclear Larmor frequency of the target nuclei. For continuous microwave driving, one requires the application on the NV of a microwave Rabi frequency equal to the nuclear Larmor frequency to achieve the Hartmann-Hahn resonance condition [3, 30]. Pulsed schemes can give access to higher harmonics of the basic modulation frequency but at the cost of reducing the effective NV-target coupling strength [12]. Furthermore, these pulsed schemes assume the application of $\pi$-pulses on the NV in time intervals that are shorter than the nuclear Larmor frequency. A failure of this condition leads to a severe reduction of the sensitivity to the NMR signal which, as we will show, scales as the inverse square of the Larmor frequency for fixed pulse duration. To restore the NMR signal, high peak power scaling proportional to the square of the Larmor frequency, as well as high average power, scaling linearly with the Larmor frequency, should be delivered. Unfortunately high microwave power lead to heating effects especially in biological samples [32], and is difficult to achieve as microwave structures that deliver the control fields experience limitations in both peak and average microwave power.

In this Letter we will first demonstrate these relationships between standard (top-hat like) $\pi$-pulses of fixed length, the power requirements and the effective coupling strength to the signal emanating from the target. Secondly, we present a solution to this problem based on suitable shaping of long $\pi$-pulses which achieve an effective dynamics that has the same effect as an instantaneous $\pi$-pulse restoring the ideal sensor-target interaction. In this manner we can extend the duration of the $\pi$-pulses and thus reducing the required microwave peak and average power to levels that are more readily accessible to current technology and more compatible with sensing applications in biological samples [8, 32]. The protocol that we present here is universal and can be incorporated into any pulse sequence used commonly in experiments in order to reduce microwave power consumption. Furthermore, we would like to stress that these methods are not restricted to the NV center in diamond which merely serves as a model system for our considerations.

Preliminaries — We consider the detection of the magnetic signals from nuclear spins precessing at the Larmor frequency as well as classical magnetic high-frequency fields, at a strong ambient magnetic field $B_z \geq 1$ T. If the Rabi frequency of the MW driving field is limited, then, for sufficiently high $B_z$, the nuclear spins or the classical signal field can complete several oscillations during a $\pi$-pulse. In the following we will analyse the reduction in sensitivity due to this effect. To this end we study the following Hamiltonian that describes an NV center interacting with an individual nuclear spin target,

$$H = DS_z^2 - \gamma_c B_z S_z - \omega_L I_z + S_z \vec{A} \cdot \vec{I} + \sqrt{2} \Omega S_z \cos(\omega t - \phi). \quad (1)$$

Here, $S_z = |\uparrow\rangle\langle\uparrow| - |\downarrow\rangle\langle\downarrow|$, $S_z = 1 / \sqrt{2} (|\uparrow\rangle \langle\uparrow| + |\downarrow\rangle \langle\downarrow| + \text{H.c.})$, $D = (2\pi) \times 2.87 \text{ GHz}$, $\gamma_c \approx - (2\pi) \times 28.024 \text{ GHz/T}$ and $\vec{A}$ is...
the hyperfine vector of the NV-nucleus interaction \cite{33}. For \( B_z \geq 1 \) T, the NV energy splitting between the \( |0\rangle \leftrightarrow |1\rangle \) transition is several tens of GHz \cite{9}, while \( \omega_n \) would reach several tens of MHz. The MW driving over the NV electron spin is \( \sqrt{2} \Omega S_z \cos(\omega t - \phi) \), where the \( \sqrt{2} \) factor is introduced for convenience. When two levels of the NV manifold, e.g. the \( |0\rangle \) and \( |1\rangle \) hyperfine spin states, are selected as the electron spin qubit basis, and by setting the driving field on resonance with that \( |0\rangle \leftrightarrow |1\rangle \) transition (i.e. \( \omega = D + |\gamma| B_z \)) one can find that in an appropriate rotating frame, see Supplemental Material \cite{54}, Eq. (1) becomes

\[
H = \frac{F(t)}{2} \sigma_{z} A_{+}^{z} I_{z} \cos(\omega_n t) + A_{+}^{z} I_{z} \sin(\omega_n t). 
\]

Here \( F(t) \) is the modulation function that appears as a consequence of the action of the MW pulse sequence, \( \omega_n \) is the nuclear resonance frequency, and \( A_{+}^{z} \) the electron-nucleus coupling constants \cite{34}. We consider periodic pulse sequences of period \( T \) such that \( F(t) = \sum F(t) \cos(\omega_n t) \) where \( \omega_m = \frac{2\pi}{T} \) and \( F(t) = \frac{2}{T} \int_{0}^{T} F(s) \cos(\omega_m s) \, ds \).

Examples of these sequences are those of the XY family \cite{35, 36} or more sophisticated schemes \cite{17, 37, 43}. In addition, we expect no influence of the other modulation functions \( F_{\perp}(t) \) and \( F_{\parallel}(t) \) if the sequence combines pulses with different phases \cite{44, 45}, this assumption will be later corroborated by our numerical simulations.

Then, for \( \omega_m = \omega_n \) (resonance condition for the \( l \)th harmonic) Eq. (3) can be approximated as \cite{34}

\[
H = \frac{f_{l}}{4} A_{+}^{z} \sigma_{z} I_{z}.
\]

Hence, it is the product of \( A_{+}^{z} \) and the Fourier \( f_{l} \) coefficient which determines the strength of the NV-nuclear interaction.

If the target is a classical field, e.g. \( \dot{B}_z \cos(\omega_n t) \), the sensor target Hamiltonian in case of resonance with the hyperfine interaction (i.e. when \( \omega_m = \omega_n \)) is \( H = \frac{|f_l|}{4} \sigma_{z} I_{z} \), where \( \Omega_\perp \) describes the amplitude of the classical signal field \cite{34}.

**Signal reduction** — For the common case of pulses in the form of top-hat functions, we can calculate the value of each coefficient \( f_{l} \) for the elementary block in Fig. 1(a).

\[
f_l = \frac{2}{T} \left[ \int_{0}^{t_1} \cos(\omega_m s) \, ds + \int_{t_1}^{t_2} \cos(\Omega_s - t_1) \cos(\omega_m s) \, ds - \int_{t_2}^{t_3} \cos(\omega_m s) \, ds - \int_{t_3}^{t_4} \cos(\Omega_s - t_3) \cos(\omega_m s) \, ds + \int_{t_4}^{T} \cos(\omega_m s) \, ds \right],
\]

where \( t_2 - t_1 = t_4 - t_3 = t_\perp \) are the lengths of the \( \pi \)-pulses, see Fig. 1(a). For instantaneous \( \pi \)-pulses, \( t_\perp = 0 \), the integrals \( \int_{t_1}^{t_3} \cos(\Omega_s - t_1) \cos(\omega_m s) \, ds \) and \( \int_{t_3}^{t_4} \cos(\Omega_s - t_3) \cos(\omega_m s) \, ds \) in Eq. (4) vanish, and \( |f_l| = \frac{|f_l|}{4} \) for odd \( l \), and \( |f_l| = 0 \) for even \( l \). When the pulse width is non-negligible one finds

\[
f_l = f_l(\alpha) = \frac{4(-1)^{l+1}/2 \cos(\alpha \pi)}{(4\alpha^2 - 1)\pi}
\]

which implies that the sensitivity under the pulse sequence decreases as \( \alpha^2 \), where \( \alpha \) equals the length of \( t_\perp = \alpha(T/l) \) measured in terms of the number of nuclear Larmor periods, see Fig. 1(b). If we are aiming for a resonance at the \( l \)th harmonic we need to set \( T \approx 2\pi / \omega_n \) (equivalent to the resonance condition \( \omega_m = \omega_n \)) where \( \omega_n = \gamma_e B_z \), \( \gamma_e \) being the nuclear gyromagnetic ratio, grows linearly with the applied magnetic field \( B_z \). From Eq. (1) we have \( t_\perp = \pi / \Omega \) and hence

\[
\Omega = \frac{\pi}{\alpha T} = \frac{\gamma_e B_z}{2\alpha}
\]

which implies for \( B = 2 \) T (5 T), a proton nuclear spin as a target \( (\gamma_e = 2\pi \times 42.57 \) MHz/T), and a peak power limited by a maximum achievable value for \( \Omega \), namely \( \Omega = (2\pi) \times 10 \) MHz, that \( \alpha \approx 4.26 \) (10.65).

In Figure 1(c) we show the rapid decay of \( f_l(\alpha) \) coe-
cients with α, for $l = 25$ (blue), $27$ (green), and $29$ (yellow) dictated by Eq. [5]. In d) we have computed the spectrum of a problem involving an NV center and a H nucleus for two values of Ω, and with $B_z = 2$T (see caption for details about the simulation). In addition, with Hamiltonian [3] one can calculate that, on resonance, the measured signal is

$$\langle \sigma_z | i \rangle = \cos [f_i(\alpha) \lambda f_i / 4]$$

with $t_f$ being the final time of the sequence [34]. Hence, if a quantum sensing experiment is conducted at high $B_z$ (which implies a large $\alpha$ to compensate for a limited $\Omega$) the obtained signal gets dramatically reduced due to the decay of $f_i(\alpha)$ with $\alpha$, as it can be seen in Fig. [1]d).

If we are interested in measuring the signal at the $l$th harmonic of the modulation frequency, the length of the π-pulses does not need to be instantaneous but may extend over many Larmor periods as long as at the end of the extended pulse its action equals that of an instantaneous pulse. This can be seen in Fig. [2] where the functions $F_i(t)$ (green flat lines), the oscillating function $\cos(\omega_{\text{int}} t)$ (solid blue lines) for $l = 11$, and two possible time intervals used for the π-pulses (superimposed clear green panels) are shown. Specifially in Fig. [2]a) $t_\pi = 2(T/l)$, while in b) $t_\pi = 4(T/l)$.

Then, if one assumes that the integral of $f_i$ could be written as

$$f_i = \frac{2}{T} \int_0^T F(s) \cos(\omega_{\text{int}} s) \, ds,$$

then one obtains that the integral of $f_i$ is equal to

$$\cos \left( \int_0^u \Omega(s) \, ds \right) \sin \left( \int_0^u \Omega(s) \, ds \right) \sin \left( \int_0^u \Omega(s) \, ds \right),$$

ie, without any contribution of the regions containing the π-pulses (see next section for an explicit construction) both cases in Figs. [2]a) and b) would lead to the same ideal value $[f_i] = \frac{1}{\pi}$, as opposed to Eq. [5]. This is because when π-pulses contain a natural number of periods of $\cos(\omega_{\text{int}} t)$ the latter expression of $f_i$ is reduced to the integral of only the yellow areas in Figs. [2] which are equal for a) and b). This offers the opportunity for extending the length of the π-pulses up until $t_\pi = (l - 1)/2(T/l)$ and hence offers the potential to reduce the average Rabi frequency and hence the intensity of the pulse significantly.

**Shaped π-pulses** — In the following we will demonstrate that by substituting the top-hat pulse shape for appropriately shaped π-pulses, we can recover the ideal $[f_i] = \frac{1}{\pi}$ scaling of the Fourier components of the filter function. This gains a factor of $\alpha^2$ in sensitivity and allows for a significant reduction in the power requirements of the pulse schemes. To this end we consider the Hamiltonian that generates the π-pulse as

$$H_p = \frac{\Omega(t)}{2} \left( |1\rangle \langle 0| e^{i\phi} + |0\rangle \langle 1| e^{-i\phi} \right) = \frac{\Omega(t)}{2} \sigma_\phi.$$  

In addition, we will keep the pulse width equal to a natural number of oscillations of $\cos(\omega_{\text{int}} t)$. As explained in the previous section this can recover the ideal values of $[f_i] = \frac{1}{\pi}$ independently of the π-pulse width, and for small values of Ω which implies a reduced power delivered to the sample. Note that shaped π-pulses have been previously considered for slow spin baths, i.e. for situations with a low value for $B_z$ [46][48].

In the rotating frame of the driving Hamiltonian ($H_p$) a $\sigma_z$ electronic operator evolves, for the first shaped π-pulse, as $\sigma_z \rightarrow \cos \int_0^t \Omega(s) \, ds \sigma_z + \sin \int_0^t \Omega(s) \, ds \sigma_\phi$, where $t < t_1 + t_\pi \equiv t_2$, and $\sigma_\phi = -i(|1\rangle \langle 0| e^{i\phi} - |0\rangle \langle 1| e^{-i\phi})$. This description is similar for any other shaped π-pulse of the sequence by replacing $t_1$ by $t_j$, the latter being the initial time time of each shaped π-pulse. Now we focus only on the part containing the $\sigma_z$ operator, i.e. the one leading to the $F_i(t)$ modulation function, because the $\sigma_\phi$ component leads to the $F_i(t)$ modulation functions that do not contribute to the spectrum if the applied sequence contains pulses over several directions [44][45]. Then, we have to find a $\Omega(s)$ that minimise, in the shaped π-pulse region, the overlap between $F_i(t) \equiv \cos \int_{t_j}^{t_{j+1}} \Omega(s) \, ds$ and $\cos(\omega_{\text{int}} u)$, this is

$$\int_{t_j}^{t_{j+1}} F_i(u) \cos(\omega_{\text{int}} u) \, du = 0,$$

with $t_{j+1} - t_j = t_\pi$. In addition, in order to have a continuous $F_i(t)$ over the whole DD sequence, the following boundary

$$F_i(t) \biggr|_{t_{j+1}} = F_i(t) \biggr|_{t_j}.$$  

**FIG. 2.** $F_i(t)$ and $\cos(\omega_{\text{int}} t)$ functions, for two different pulse widths (clear green). a) $t_\pi = 2(T/l)$ and b) $t_\pi = 4(T/l)$, in both cases $l = 11$. In the π-pulse regions it is remarked the center of each finite-width π-pulse with a vertical black line. The latter would correspond with the locations of the instantaneous π-pulses. The areas in yellow contribute to the value of $f_i$, while grey areas (positive oscillations) are cancelled by blue areas (negative oscillations).
conditions are needed: $F_z(t_j) = (-1)^{j+1}$ and $F_z(t_{j+1}) = (-1)^{j}$, for the $n$th applied shaped $\pi$-pulse.

These conditions have an infinite number of solutions and here we present as an example the analytical solution

$$F_z(u) = \cos \left[ \frac{\pi}{2\gamma} (u - t_j) \right] - \beta e^{-\frac{(u-t_j)^2}{2\gamma^2}} \sin \left[ \frac{2\alpha}{t_\pi} (u - t_j) \right], \quad (9)$$

where $\beta$ is a parameter that will be fixed with Eq. (8). For the first shaped $\pi$-pulse $t_p$ is the middle point in between $t_1$ and $t_2$, or between $t_3$ and $t_4$ for the second one. The $\alpha$ and $\gamma$ parameters can be advisedly adjusted, such that their value determine the pulse length and maximum intensity of the employed $\Omega(t)$ in Eq. (7). The above solution is valid for $\alpha$ equal to $1, 2, 3, \ldots$ i.e. when the shaped $\pi$-pulse contains a natural number of periods of $\cos (\omega_{\text{B}} t)$. Equation (8) leads to the following condition for $\beta$, see [34], $\beta = 4 \frac{\sqrt{\omega_{\text{B}}}}{(4\omega_{\text{B}} - 1)\sqrt{\pi}} \left[ 1 - \exp \left(-\frac{4\omega_{\text{B}}^2}{\pi^2} \right) \right]$ where $\gamma$ and $\alpha$ are related as $\gamma = t_p/c$. Once $\beta$ is chosen, one can calculate $\Omega(t) = \partial_t \arccos [F(t)]$ by inverting $F_z(t) = \cos \left[ \int_{t_j}^{t} \Omega(s) \, ds \right]$.

Fig. 3a shows the evolution of $F_z(t)$ from $-1$ to $+1$ that results from the application of a $\pi$-pulse with a constant $\Omega$, i.e. a standard top-hat pulse as those in Fig. 1 b), while Fig. 3b) corresponds to $F_z(t)$ for the shaped $\pi$-pulse whose $\Omega(t)$ is shown in c). In [34] we can see a whole period of $F_z(t)$ resulting from the application of $\Omega(t)$ in c). In d) we have computed numerically the response versus frequency that results from a system at a magnetic field of $B_z = 1.5$ T involving a NV center and two H nuclei. The hyperfine vectors are $A_1 = (2\pi) \times [0, 14.43, -46.63]$ kHz and, $A_2 = (2\pi) \times [-10.93, 6.31, -42.34]$ kHz. The blue line corresponds to the signal obtained when 1440 ideal instantaneous $\pi$-pulses have been applied (final time of this sequence is $t_f \approx 0.71$ ms). The black squares represent the signal that emerges when our shaped pulses in Fig. 3(c) are applied. Here we use the sequence [XYYYYYYYY] for its convenient robustness conditions against errors on the MW control [35], with $N = 180$ and X (Y) a shaped pulse with phase $\phi = 0$ ($\phi = \frac{\pi}{2}$), see Eq. (7). This signal overlaps perfectly with the ideal one which employs instantaneous $\pi$-pulses. The yellow line corresponds to the application of standard top-hat $\pi$-pulses with $\Omega = (2\pi) \times 20$ MHz, while the red one uses $\Omega = (2\pi) \times 40$ MHz. In these two cases, the contrast of the harvested signal is seriously reduced with respect to the one obtained with our shaped pulses which employ a maximum of $\Omega = (2\pi) \times 6.4$ MHz, i.e. a reduced peak and average power, see later.

In Fig. 4 the same effect is shown for the case of a classical signal target. We here demonstrate that the contrast reduction appears even at not so high $B_z$ fields (note we used a classical signal with frequencies that would correspond to H nuclei with a Larmor frequency akin to $B_z \approx 0.5$ T). This becomes evident by inspecting Eq. (9) where it gets clear that finding a non negligible value for $\alpha$, which would lead to a decreasing $f(\alpha)$ coefficient, depends on the ratio between $B_z$ and $\Omega$. In this manner, a situation where the MW source cannot deliver high power to the sample, i.e. we have access only to low values for $\Omega$, would unavoidably lead to poor signal contrast.

However, the appropriate application of shaped $\pi$-pulses leads to an undistinguishable overlapping signal (squares) with respect to the ideal spectrum (blue line). The red line with almost negligible contrast has been computed with top hat pulses corresponding to $\Omega = (2\pi) \times 10$ MHz. We used the same [XYXYYYYYY] sequence for $N = 5$. That is 40 pulses, shaped and top-hat, have been applied. The final time of the sequence is $t_f \approx 0.03$ ms. Note that shaped pulses are generated with a maximum of $\Omega = (2\pi) \times 8.12$ MHz.

Finally, in order to achieve similar results to the ideal case in Fig. 3(d) with finite width of top-hat pulses, a value for $\Omega$ of, at least, $\Omega = (2\pi) \times 100$ MHz is needed. The latter is much larger than the maximum of $\Omega(t)$ in Fig. 3(c), i.e. $(2\pi) \times 6.4$ MHz, employed by our shaped pulse which implies that our method requires a much lower peak power. More specifically, the square ratio (peak power ratio) of these two quantities is $(2\pi) \times 100 / (2\pi) \times 6.4)^2 \approx 244$ which certifies that our method is energy efficient. In addition, the ratio between the average energy required by the two approaches is $E_{\text{top-hat}} / E_{\text{shaped}} = 27.47$ [34]. A similar situation occurs in Fig. 4. Here for obtaining the same contrast as in the ideal case the finite width top-hat pulses require at least $\Omega = (2\pi) \times 50$ MHz, while the maximum value of $\Omega(t)$ is $(2\pi) \times 8.12$ MHz. The latter leads a peak power ratio $\approx 38$ while $E_{\text{top-hat}} / E_{\text{shaped}} = 10.63$.

Conclusions — We have considered the problem of quantum sensing at high magnetic fields which leads to high frequency signals and demonstrated that the finite length of standard top-hat pulses in dynamical decoupling sequences lead to a rapid decrease of sensitivity with signal frequency. We present a general solution to this problem using shaped pulses which allow for pulses extending over many Larmor periods and hence for significant reductions in the required microwave power. The robustness of the shaped pulses facilitate their experimental realisation [49]. We chose a NV center in diamond as the model system, but our method is general and applicable to other magnetic defects.

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Supplemental Material: \hspace{1em} \textbf{Shaped Pulses for Energy Efficient High-Field NMR at the Nanoscale}

I. NV-NUCLEUS HAMILTONIAN

The Hamiltonian (1) of the main text, in the rotating frame of the electron-spin free-energy term, $DS_z^2 - \gamma_e B_z S_z$, reads

$$ H = -\omega_n \hat{\omega}_n \cdot \hat{F} + \frac{1}{2} \sigma_z \hat{F} + \frac{\Omega}{2} \langle 1 \rangle \langle 0 \rangle |e^{i\phi} + |0 \rangle \langle 1 |e^{-i\phi} \rangle. $$

(S1)

Here, we have eliminated any electron spin component containing the $| - 1 \rangle$ state because, as the MW driving is tuned with the $|0 \rangle \leftrightarrow |1 \rangle$ transition, the $| - 1 \rangle$ component gets no populated. The $\hat{\omega}_n$ vector is $\hat{\omega}_n = (-\frac{1}{2} A_x, -\frac{1}{2} A_y, \omega_L - \frac{1}{2} A_z)$, with $\vec{A} = \frac{\omega_L}{2 \gamma_L} [\vec{z} - 3 \hat{x} \vec{B} \cdot \vec{r}_{\perp}]$ being the hyperfine vector (note that we are assuming dipole-dipole interactions between the NV and the nuclear spin) $\omega_L = |\hat{\omega}_n|$ is the resonance frequency of the nucleus which is shifted from the Larmor frequency because of the hyperfine field, and $\hat{\omega}_n = |\hat{\omega}_n|/\omega_L$.

In a new rotating frame with respect to (w.r.t), both, $-\omega_n \hat{\omega}_n \cdot \hat{F}$ and to the MW driving, one can find that

$$ H = \frac{F_z(t)}{2} \sigma_z \hat{F} + \left[ (\hat{A} - \hat{\vec{A}} \cdot \hat{\omega}_n \hat{\omega}_n) \cos (\omega_n t) + \hat{\omega}_n \times \hat{\vec{A}} \sin (\omega_n t) + \hat{\vec{A}} \cdot \hat{\omega}_n \hat{\omega}_n \right], $$(S2)

where $F_z(t)$ is the modulation function, see [S1], that appears as a consequence of the applied $\pi$-pulses. As $F_z(t)$ will alternate between $+1$ and $-1$ the constant term $\hat{\vec{A}} \cdot \hat{\omega}_n \hat{\omega}_n$ can be averaged out. Then, the above Hamiltonian can be written as

$$ H = \frac{F_z(t)}{2} \sigma_z \left[ A^+_x I_x \cos (\omega_n t) + A^+_y I_y \sin (\omega_n t) \right], $$(S3)

where $A^+_x = |\hat{A} - \hat{\vec{A}} \cdot \hat{\omega}_n \hat{\omega}_n| A^+_y = |\hat{\omega}_n \times \hat{\vec{A}}|$, the $\hat{x}$ and $\hat{y}$ directions are $\hat{x} = (\hat{A} - \hat{\vec{A}} \cdot \hat{\omega}_n \hat{\omega}_n)/A^+_x$, $\hat{y} = \hat{\omega}_n \times \hat{\vec{A}}/A^+_y$, and $I_x = \hat{I} \cdot \hat{x}$, $I_y = \hat{\vec{I}} \cdot \hat{y}$. In this manner, Eq (S3) of this supplemental material coincides with Hamiltonian (2) in the main text.

II. THE CASE OF A CLASSICAL FIELD

The situation is similar when we want to detect classical signals of the form $\vec{B}_c \cos (\omega_c t)$. In this case, instead of the initial Hamiltonian in Eq. (1) of the main text we would have

$$ H = DS_z^2 - \gamma_c B_z S_z + \Omega_2 S_z \cos (\omega_2 t) + \sqrt{2} \Omega S_z \cos (\omega t - \phi), $$

(S4)

where the target signal Rabi frequency is $\Omega_2 = \gamma_c \vec{B}_c \cdot \vec{z}$. The other components of the signal field $\vec{B}_c \cos (\omega_c t)$ can be averaged out because $\omega_c$ is not on resonance with any of the two possible NV electron spin transitions. More specifically, if we assume that $\vec{B}_c \cos (\omega_c t)$ is generated by a spin cluster, $\omega_c$ would be on the range of several MHz for $B_c$ around a few teslas, while NV transitions require several the Gigahertz to be excited.

In the rotating frame of $DS_z^2 + |\gamma_c B_z S_z|$ and setting on resonance the driving frequency $\omega$ with, for example, the $|0 \rangle \leftrightarrow |1 \rangle$ transition, we have

$$ H = \frac{\Omega_2}{2} \sigma_z \cos (\omega_c t) + \frac{\Omega}{2} \langle 1 \rangle \langle 0 \rangle |e^{i\phi} + |0 \rangle \langle 1 |e^{-i\phi} \rangle, $$

(S5)

once we have eliminated constants and any term including the $| - 1 \rangle$ NV spin component. The use of a standard scheme, as the Hartmann-Hahn double resonance condition [S2], to make interact the NV with the classical field is limited to low values of $\omega_c$. This is because it is required to hold $\omega_c = \Omega$ and the driving power, here reflected in the value of $\Omega$, could be limited. The latter can be easily seen by noting that, in a rotating frame with respect to $\frac{\Omega}{2} (|0 \rangle \langle 0 | + |1 \rangle \langle 1 |)$ we set $\phi = 0$ and $\Omega$ is constant, the above Hamiltonian is

$$ H = \frac{\Omega_2}{4} (|+\rangle |+\rangle e^{i\Omega t} + |\rangle |\rangle e^{-i\Omega t} (e^{i\omega_c t} + e^{-i\omega_c t})), $$

(S6)

where $|\pm\rangle = \frac{1}{\sqrt{2}} (|\uparrow\rangle \pm |\downarrow\rangle)$. Now one can see that, unless the condition $\Omega = \omega_c$ holds, the previous Hamiltonian is entirely time-dependent and would average to zero because of the rotating wave approximation.
FIG. S1. $F_z(t)$ and $\cos(l\omega_m t)$ functions for the 63rd harmonic, i.e. $l = 63$, and for $\alpha = 30$.

Hence, one should consider the use of pulsed schemes. In this case, Eq. (S5) can be written in the rotating frame of the MW driving $\frac{\Omega}{2}|1\rangle\langle 0|e^{i\phi} + |0\rangle\langle 1|e^{-i\phi}$ with $\Omega$ applied stroboscopically, as

$$H = \frac{\Omega}{2} F_z(t) \sigma_z \cos(\omega_s t). \quad (S7)$$

Now, as $F_z(t) = \sum_l f_l \cos(l\omega_m t)$, and in the case of $l\omega_m = \omega_s$ (i.e. resonance condition for the $l$th harmonic) the above Hamiltonian after eliminating fast rotating terms is

$$H = \frac{\Omega_s}{4} f_l \sigma_z, \quad (S8)$$

which is the equation we find in the main text.

III. ENERGY CONSIDERATIONS

The rate of energy transport, i.e. energy per unit of time and unit of area, that an electromagnetic wave carries is given by the Poynting vector

$$\vec{S} = \frac{1}{\mu_0} \vec{E} \times \vec{B}. \quad (S9)$$

One can see that the units of $\vec{P}$ are $[\vec{P}] = \frac{J}{s^2 m^2}$. Note that in the literature the Poynting vector is typically referred as $\vec{S}$, but here $\vec{S}$ is already used for the NV-electronic spin.

We will consider the external driving acting on the sample as plane waves because we use MW radiation which has a long wavelength. The applied $\pi$-pulses are generated through the Hamiltonian

$$H = |\gamma_e| B(t) \cdot \vec{S} = |\gamma_e| B_x(t) S_x, \quad (S10)$$

where without any loss of generality we have assumed that the $B_x$ field is polarised in the $x$ direction. We can compute the associated $\vec{E}(t)$ field by using the Maxwell equation

$$\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}. \quad (S11)$$

A. Square $\pi$-pulses

For the case of square $\pi$-pulses we have (note that also without any loss of generality we selected $\hat{x}$ as the propagation direction) $\vec{B}(y, t) = B_x \cos(\omega t - ky + \phi) \hat{x}$, which would be applied on the NV position, namely $y_0$. The later would simply lead to a reinterpretation of the phase $\phi$, i.e. we just have to make the change $\phi \rightarrow \phi$ to achieve the driving term of Eq. (1) in the main text. In addition, for square $\pi$-pulses $B_x$ is constant, then we have

$$\partial_y E_z(y, t) = -\frac{\partial}{\partial t} B_x \cos(\omega t - ky + \phi), \quad (S12)$$
which leads to

\[ E_\omega(y, t) = c B_y \cos(\omega t - ky + \phi). \]  

(S13)

Finally, the Poynting vector reads (note that we provide the quantity \( |\hat{P}| \), but it can be easily seen that the energy flows in the \( \hat{y} \) direction)

\[ |\hat{P}| = \frac{c}{\mu_0} B_z^2 \cos^2(\omega t - ky + \phi) = \frac{c}{\mu_0} B_z^2 \cos^2(\omega t + \phi) \]  

(S14)

where the last equality assumes that we are calculating the energy flow in the \( y_0 \) position, i.e. the NV position.

As expected the energy per unit of time and area (instantaneous energy or peak power), grows as \( B_z^2 \propto \Omega^2 \) i.e. it is proportional to the square of the Rabi frequency. On the other hand, the energy per \( \pi \)-pulse, i.e. the average energy, requires to integrate Eq. (S14) between 0 and \( t_\pi = \frac{1}{2\pi} \). In this manner we have that the energy per unit of area that the external driving introduces with a top-hat \( \pi \)-pulse (average energy) is

\[ E_{\text{top-hat}} = \int_0^{t_\pi} |\hat{P}| \, dt = \frac{c}{\mu_0} \frac{2\Omega^2}{\gamma_e^2} \int_0^{t_\pi} \cos^2(\omega t - ky + \phi) \, dt = \frac{c}{\mu_0} \frac{2\Omega^2}{\gamma_e^2} \left[ \frac{1}{2} t_\pi + \frac{1}{4\omega} \left( \sin(2\omega t_\pi + 2\phi) - \sin(2\phi) \right) \right] \approx \frac{c}{2\mu_0} \frac{\Omega^2}{2\gamma_e^2} \]  

(S15)

Note that, according to our convention in Eq. (1) of the main text, we have \( \sqrt{2}\Omega = B_z\gamma_e \). Finally, and as \( t_\pi = \frac{1}{2\pi} \) we recover the intuition that the energy per \( \pi \)-pulse is \( \propto \Omega \). More specifically we get

\[ E_{\text{top-hat}} \approx \frac{c}{2\mu_0} \frac{\Omega^2}{2\gamma_e^2}. \]  

(S16)

### B. Shaped \( \pi \)-pulses

The situation is different if we consider our shaped \( \pi \)-pulses. Here the employed magnetic field to generate the driving is \( \vec{B}(y, t) = B_z(t) \cos(\omega t - ky + \phi) \, \hat{x} \) where \( B_z(t) \) is now time modulated. Consequently, we have that

\[ E_\omega(y, t) = -\int \frac{\partial}{\partial t} B_z(t) \cos(\omega t - ky + \phi) \, dy = \frac{\sqrt{2}}{k\gamma_e} \frac{\partial}{\partial t} \left[ \Omega(t) \sin(\omega t - ky + \phi) \right] \]  

(S17)

and the energy density, i.e. \( |\hat{P}| \), is

\[ |\hat{P}| = \frac{c}{\mu_0} \frac{2}{\gamma_e^2} \Omega^2(t) \cos^2(\omega t + \phi) + \frac{2}{\mu_0 k\gamma_e^2} \Omega(t) \left[ \frac{\partial}{\partial t} \Omega(t) \right] \sin(\omega t + \phi) \cos(\omega t + \phi), \]  

(S18)

while the \( \pi \)-pulse energy is

\[ E_{\text{shaped}} = \int_0^{t_\pi} |\hat{P}| \, dt = \int_0^{t_\pi} \frac{c}{\mu_0} \frac{2}{\gamma_e^2} \Omega^2(t) \cos^2(\omega t + \phi) \, dt + \int_0^{t_\pi} \frac{2}{\mu_0 k\gamma_e^2} \Omega(t) \left[ \frac{\partial}{\partial t} \Omega(t) \right] \sin(\omega t + \phi) \cos(\omega t + \phi) \, dt \]

\[ = \frac{2c}{\mu_0 \gamma_e^2} \int_0^{t_\pi} \Omega^2(t) \cos^2(\omega t + \phi) \, dt + \frac{2}{\mu_0 k\gamma_e^2} \int_0^{t_\pi} \Omega(t) \left[ \frac{\partial}{\partial t} \Omega(t) \right] \sin(\omega t + \phi) \cos(\omega t + \phi) \, dt, \]  

(S19)

note that the above expression can be numerically integrated once the form of \( \Omega(t) \) is known.

### IV. THEORETICAL CALCULATION OF THE NUCLEAR SIGNAL

From Hamiltonian (3) of the main text and assuming as initial state of the NV-nucleus system \( \rho_0 = \frac{1}{2} (\mathbb{1} \otimes \sigma_z) \otimes \mathbb{I} \), i.e. the NV is initialised in an equal superposition of the \(|0\rangle \) and \(|1\rangle \) states, and the nucleus is in a thermal state that is represented here by the \( 2 \times 2 \) identity operator \( \mathbb{1} \). Then the time dependent coherency, \( \langle \sigma_z \rangle_t \), of the NV electron spin is

\[ \langle \sigma_z \rangle_t = \frac{1}{4} \text{Tr} \left[ \rho_t e^{i [f(t) A_z^+ t_f / 4 \sigma_z] / 4} (\sigma_z \otimes \mathbb{1}) \right] = \cos(f_t(\alpha) A_z^+ t_f / 4). \]  

(S20)
V. INTEGRATING $F_z(u)$

The condition in Eq. (8) of the main text when applied to the solution in (9) leads to the two following integrals

$$\int_{t_1}^{t_2} \cos \left( \frac{\pi}{t_\pi} (u-t_1) \right) \cos \left[ k \frac{2\pi}{T} u \right] du = t_\pi \left[ \frac{1}{(2\alpha + 1)\pi} + \frac{1}{(2\alpha - 1)\pi} \right]$$  \hspace{1cm} (S21)

$$\int_{t_1}^{t_2} \exp \left[ - \frac{(u-t_p)^2}{2c^2} \right] \sin \left( \frac{2\pi\alpha}{t_\pi} (u-t_1) \right) \cos \left[ k \frac{2\pi}{T} u \right] du \approx c \sqrt{\frac{\gamma}{2}} \left[ 1 - \exp \left( -\frac{8\alpha^2 \pi^2}{\gamma^2} \right) \right]$$  \hspace{1cm} (S22)

with $c = \frac{t_\pi}{\gamma}$. For solving the last integral we have used the following relations

$$\int_{-\infty}^{+\infty} e^{-(x-b)^2/2c^2} dx = \sqrt{2\pi}\vert c \vert \sqrt{\pi}$$

$$\int_{-\infty}^{+\infty} e^{-ax^2} \cos (bx) dx = \sqrt{\frac{\pi}{a}} e^{-b^2/4a}.$$  \hspace{1cm} (S23)

VI. ONE PERIOD OF $F_z(t)$ AND $\cos (\omega_m t)$

In Fig. S1 we can observe one period of both the oscillating function $\cos (\omega_m t)$ and the modulation function $F_z(t)$ that appears as a consequence of the shaped pulses in Fig. 3 c) of the main text. In clear green, it is showed the space in which each $\pi$-pulse is spanned. This form of $F_z(t)$ assures the achievement of the ideal value of $\vert f \vert = \vert \frac{4\pi}{T} \int_0^T F_z(s) \cos (\omega_m s) ds \vert = \vert \frac{4\pi}{63\pi} \vert = \vert \frac{4}{63\pi} \vert$.

VII. SEQUENCE ROBUSTNESS

In the main text we used an XY-8 sequence which is commonly used in experiments because of its robustness against errors in the control MW field. In Fig. S2 we compare the signal for a sequence with ideal instantaneous pulses (blue line) and shaped pulses with an error of 1% in the amplitude of the Rabi frequency (squares) [S3]. Note we ordered the shaped-pulse-sequence according to an XY-8≡[XYXYYXYX] scheme. We can observe that, even under these error conditions, the signal obtained with imperfect shaped pulses overlaps with the ideal signal. The orange line is the signal obtained with imperfect shaped pulses, again with a 1% of Rabi frequency deviation, but the pulses are applied following a CPMG scheme. The latter means that we are repeating the sequence [XXXXXXXXX] that does not include pulses with alternating phases. In this case we can observe, see Fig. S2 that the accumulated errors totally disturb the signal.

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