Macroscopic Hyperpolarization Enhanced with Quantum Optimal Control

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Hyperpolarization of nuclear spins enhances nuclear magnetic resonance signals, which play a key role for imaging and spectroscopy in the natural and life sciences. This signal amplification unlocks previously inaccessible techniques, such as metabolic imaging of cancer cells. In this work, electron spins from the photoexcited triplet state of pentacene-doped naphthalene crystals are used to polarize surrounding protons. As existing strategies are rendered less effective by experimental constraints, they are replaced with optimal control pulses designed with RedCRAB. In contrast to previous optimal control approaches, which consider one or two effective nuclei, this closed-loop optimization is macroscopic. A 28% improvement in signal and 15% faster polarization rate is observed. Additionally, a strategy called Autonomously-optimized Repeated Linear Sweep (ARISE) is introduced to efficiently tailor existing hyperpolarization sequences in the presence of experimental uncertainty to enhance their performance. ARISE is expected to be broadly applicable in many experimental settings.

I. INTRODUCTION

Sensitive Nuclear Magnetic Resonance (NMR) spectroscopy and Magnetic Resonance Imaging (MRI) applications are a key driver in research areas from life sciences through material science to quantum computing. The feasibility and sensitivity of such experiments critically depends on the polarization of the utilized spins. Dynamic Nuclear Polarization (DNP) techniques have been shown to increase NMR signals by multiple orders of magnitude [1], enabling previously inaccessible imaging techniques [2]. DNP transfers the polarization from highly polarized electron spins to the target species of nuclear spins [3] used for NMR protocols. Electron spins are polarized, for example, by thermalization at low temperatures and high magnetic fields or by optical polarization of atoms and suitable molecules in gases, liquids, and solids [1, 4–11]. In this work, the electron spins of photoexcited triplet states in pentacene-doped naphthalene are used as the source of polarization, and the proton spins of naphthalene as the target. This system, shown in Fig. 1b, exhibits unique properties. In its ground state, the electron spin is in a singlet state and therefore the host crystal is free of paramagnetic defects. Consequently, proton relaxation times of 50 hours and above have been demonstrated at 77 K and 0.5 T [12]. In its metastable triplet state, the pentacene molecule exhibits a highly polarized electron spin with favorable lifetimes. Together with surrounding nuclear spins, this forms a central spin system that resembles other well-known systems like NV centers in diamond or phosphorous in silicon. This quantum resource for DNP leads to record values of 80% proton polarization [13], which amounts to a polarized proton concentration of 50 M. Exemplary applications of these nuclear spin polarized crystals are portable neutron spin filters in neutron scattering experiments [12, 14] and polarization agents for NMR spectroscopy [15, 16]. Under typical operating conditions (e.g., high magnetic field), electron and nuclear spins are mutually off resonant, prohibiting direct polarization transfer. This is then achieved via advanced spin control methods, like DNP. Real-world experimental constraints like material quality, field inhomogeneities, and limited power and bandwidth usually impair the ideal performance of existing DNP methods. Under such constraints, the maximum achievable polarization is reduced and the time to reach a certain polarization increases.

The goal of this work is to optimize the DNP transfer process by maximizing the proton polarization. Correspondingly, a new multi-step protocol is introduced called Autonomously-optimized Repeated Linear Sweep (ARISE).

In the case where the heterogeneity among spins is suf-
FIG. 1. Experimental realization. a) Schematic of the in-house polarizer device. The sample (red) is mounted on a sample stick, which allows moving it between a MW cavity and an NMR coil inside a magnetic field at cryogenic temperatures. b) Level scheme of pentacene (electron spin) and naphthalene-based protons (nuclear spins), including the effect of laser excitation (green) and natural decay (blue). Spin diffusion to external nuclear spins [17] is indicated. c) 30 s of hyperpolarization show a clear signal enhancement compared to a 1 h thermal build-up, the thermal signal is scaled by a factor of 50 to emphasize its faint polarization peaks. d) Schematic visualization of the pulse sequence, consisting of a laser pulse for triplet state creation and a MW pulse (of variable frequency) for polarization transfer to the nuclear spins. This basic block is repeated with a repetition rate of 1 kHz (i.e., 30,000 repetitions are performed in 30 s). After the polarization, the sample is shuttled into the NMR coil, where the magnetization is measured. An integral over the detected proton polarization is passed to RedCRAB, which provides the shape of the next MW pulse.

sufficiently small, they are all equally well controllable. As a result, techniques like nuclear orientation via electron-spin locking (NOVEL) [18, 19] can be employed to transfer polarization. As the environmental complexity and inhomogeneity increases, other techniques are needed. Transferring polarization while counteracting a broad electron Spin Resonance (ESR) is done with the so-called “Integrated Solid Effect” (ISE) [20, 21]: After the electron spin initialization, either a linear magnetic field sweep is performed while the sample is driven by a constant microwave (MW) field $B_1$, or a linear MW frequency sweep is performed at a static magnetic field. The ISE method is notable for both its simplicity and robustness and has been shown to reach up to 80% total nuclear polarization in naphthalene under optimized conditions (e.g., liquid He cooling, sample quality) [13]. It has also been applied to NV centers in diamond at room temperature [11, 22–24]. While optimizing DNP sequences on a model, i.e. performing open-loop Quantum Optimal Control (QOC), is one method to recover some of their performance [25–27], another is to employ closed-loop QOC by allowing an algorithm to directly control the experiment (shown in Fig. 1d) [28–32]. The latter approach is particularly appealing when the experimental setting is very complex or impossible to accurately model. This is the first time that closed-loop QOC has been applied to optimize DNP sequences. Due to the complex molecular environment, coupled with experimental constraints, the system’s true transfer function (i.e., from optically initialized pentacene electron spins to macroscopic proton polarization throughout the naphthalene crystal) is obscured, making accurate simulation difficult. The MW DNP sequence is improved via closed-loop QOC to increase the macroscopic proton polarization.

Many advances in quantum technology were only possible due to the design of sophisticated control strategies using methods of QOC [28–32]. Established methods of QOC include gradient-based algorithms like GRAPE (gradient ascent pulse engineering) [33, 34], the Krotov algorithm [35, 36] or gradient-based algorithms based on automatic differentiation [37], as well as algorithms based on an expansion of the control pulse into a truncated basis like the dressed Chopped RAndom Basis (dCRAB) algorithm [32, 38, 39], typically coupled with direct search maximization algorithms. This pulse expansion ansatz can also be combined with the gradient approach [40–42]. The dCRAB algorithm is readily applicable to closed-loop control as it can be inte-
grated directly with an experiment, allowing the user to
treat the system as a black-box. For this purpose, the
dCRAB algorithm was implemented in the QOC soft-
ware packages Remote-dCRAB (RedCRAB) [43–46] and
its open-source version Quantum Optimal Control Suite
(QuOCS) [47]. Recently, RedCRAB enabled automatic
calibration of quantum gates [45] and robust sensing op-
erations [48] with NV centers in diamond, optimization of
BEC creation in ultracold atoms [46] and the creation of
a 20-atom Schrödinger cat state with Rydberg atoms
in an optical lattice [49].

In this work, the efficiency of the overall proton polariza-
tion process is increased by optimizing the DNP transfer
process using closed-loop QOC. To guide the algorithm
towards a solution which produces a strongly increased
signal, it is helpful to provide a good initial guess. This
is done through the application of the ARISE protocol
introduced in this work. It provides a systematic ap-

troach to the improvement of ISE-like linear sweep DNP
sequences in the presence of an unknown experimental
transfer function. In Section II the experimental pro-
cedure is described (Section II.1) and the polarization
results and pulses are introduced (Section II.2). In Sec-
tion III the results are discussed and put into context.
The measurement techniques are explained in more de-
tail in Section IV.1 and a short overview of the dCRAB
method is given in Section IV.2. The theoretical model
that was developed and used for comparison is explained
in Section IV.3.

II. RESULTS

A pentacene-d14 naphthalene crystal is placed in a mag-
netic field of 230 mT at around 130 K, chosen because this
is the limit of the polarizer, and then a ∼ 500 mW, 600 ns
laser pulses initialize the pentacene molecules into their
metastable spin-polarized triplet state $T_1$ (see Fig. 1a)
via the singlet state $S_1$ from which it decays to the lower
$T_1$ triplet via inter-system crossing (ISC) [50]. The pulse
repetition rate is fixed at 1 kHz. Depending on the oc-
cupation of the $T_1$-states, the pentacene returns to its
ground state $S_0$ after 80-180 µs. During this intermedi-
ate time, a MW DNP sequence transfers electron spin po-
larization to the densely packed proximal proton spins.
Strong dipolar coupling among protons distributes po-
larization throughout the entire crystal via spin diffu-
sion. The macroscopic polarization is measured via
NMR spectroscopy after a 30 s buildup (i.e., 30,000
cycles of electron spin initialization and DNP transfer).
Starting from an external linear sweep (similar to ISE),
and altering the amplitude and phase of the MW pulse
via the ARISE protocol, using RedCRAB, this polariza-
tion is optimized. Closed-loop QOC implicitly accounts
for all experimental conditions influencing the transfer
from optically initialized pentacene spins to macroscopic
polarization.

These could be, for example, the different lifetimes in the
metastable state for different electron spin states or vari-
ations of the pentacence lifetimes throughout the crystal
which might impact the final polarization. Another poten-
tial source of uncertainty could be the strong vari-
ation of couplings between the electron and surrounding
proton spins or the distribution of polarization via spin
diffusion during and after the MW DNP sequence. Fluc-
tuations in the experimental setup might also play a role,
as bandwidth limitations of microwave equipment, spa-
tial and spectral MW field variation inside the MW res-
onator, and spatial variation of laser intensity can also
impact the efficiency. Additionally, it is challenging to
control the amplitude of the MW field while its frequency
is scanned across the resonance. Black-box (closed-loop)
QOC does not directly incorporate variations in these
parameters, whose role in polarization transfer is not un-
derstood, but if they play a role it can be captured by
such an optimization. Importantly, some of these influ-
ences are very hard to predict theoretically. The ARISE
protocol results in a 26% increase in the hyperpolarized
signal observed alongside a 15% higher polarization rate.

As a result, the optimal sequence reaches 98% of the
maximum polarization achieved with the linear external
sweep in just 3.36 hours, instead of 9 hours (see Fig. 3).
This decrease by a factor of 2.6 enables multiple follow-up
experiments per day.

Additionally, by examining the shape of the optimized
pulse and fitting its main features, a simplified analytical
function is obtained describing the pulse (shown in [51],
labelled “Fitted Optimal”). This retains most of the en-
hanced performance of the optimized sweep.

II.1. Experimental Realization

The experimental results are obtained in an in-house po-
larizer device, shown in Fig. 1a, consisting of an optically
accessible MW cavity inside an electromagnet operating
at fields up to 800 mT. Within the MW cavity, photo-
excited triplet states are created using a 556 nm pulsed
laser with a repetition rate of 1 kHz delivering 0.35 mJ op-
tical power in a 588 ns laser pulse every 1 µs and setting
the timing of experiments. With the sample positioned
inside the MW cavity, the spin state is manipulated us-
ing a MW pulse in between laser pulses. Sophisticated
pulse shapes can be sampled and uploaded to an Arbi-
trary Waveform Generator (AWG) using the experimen-
tal control software Qudi [52]. The sample is attached to
a holder that allows it to be shuttled into an NMR coil,
which is located next to the MW cavity. Here, an NMR
spectrometer (Magritek Kea2) is used to read out the
polarization of the proton spins using a 1 Pulse measure-
ment. This round-trip takes approximately 45 seconds
from the pulse engineered by the RedCRAB software to
the NMR measurement.

An optional 532 nm continuous wave laser additionally
allows the readout of the pentacene’s electronic spin state
optically: it is not used during closed-loop optimizations,
but during the pentacene spin characterization experi-
ments. Cooling of the sample is provided by a nitrogen
FIG. 2. Implementation of a selection of polarization pulses. From left to right, the figure presents the following MW pulse schemes on the resonator: The externally applied linear sweep, a linear sweep-based QOC-generated pulse, sinusoidal sweep of the detuning, a corresponding QOC-generated pulse. The first row gives the detuning applied by the drive with respect to time. The orange area comprises the window in which the Hartmann-Hahn resonance condition lies ($\Delta_2 = \omega_2^2 - \Omega^2$). The second row shows the Rabi frequency as applied externally (dashed), the field inside the cavity (solid blue), and the resonance condition for the given detuning (thin, orange). The last row shows how the polarization builds up over the course of the pulse. Experimental values (exp.) are shown in blue, theoretical values (sim. for simulation) in gray. The solid black line indicates the final polarization.

A gas flow system, which allows precise control of the temperature from 130 K to above room temperature. The measurements are carried out at the lower limit of 130 K. A naphthalene crystal doped with pentacene grown in-house provides the electron spin system used as the polarization target.

II.2. Polarization Results

The optimization directly adjusts the pulse phase for experimental convenience, but as the detuning modulation $\Delta$ contains the same information and connects directly to the system dynamics, it is displayed in Fig. 2 instead. The first row of Fig. 2 shows the detuning modulation $\Delta$ as a function of time during the pulse. In the second row, the y-axis shows the amplitude $\Omega$ during the pulse for both the externally applied field and the internal cavity field. The Hartmann-Hahn resonance [53], shown in orange, is calculated using the time-dependent detuning assuming the target spin is a proton. In the third row of Fig. 2, experimental data and simulation are compared, showing how the polarization builds up during the pulse. The first initial guess pulse is an ISE-like linear sweep whose parameters (amplitude, sweep rate and duration) had already been manually tuned on the experimental setup. This pulse serves as the benchmark against which the optimized pulses are compared both in the experiment and in the simulation. The optimization of that guess results in the pulse labelled “Optimal (Linear)” which shows a relative polarization improvement of approximately 19%. The evolution of the Figure of Merit (FoM) during the search for an optimized pulse and the comparison between the initial and the optimized version are shown in Fig. 4.

The “Optimal (Linear)” pulse transfers the majority of its polarization during the first 10 $\mu$s. It is notable that the detuning is oscillating during that time, and it crosses the cavity resonance several times. The algorithm slows the sweep down as the detuning approaches the resonance. Both features appear in multiple optimization outcomes. Arguably, if some electron population is left untransferred, subsequent sweeps through the resonance in both directions (from positive to negative detuning and back) can serve as additional opportunities for the polarization of more weakly coupled nuclear spins.

After analyzing the effect of the amplitude and phase of the pulse independently (see supplementary information for more details [51]), the MW amplitude is kept constant in later optimizations. To further explore the idea that repeated sweeps through the resonance are beneficial, pulses with phase oscillations that use a range of frequencies and pulse durations are tested, see the supplementary material [51] for more details. The “Sinu-
The “Sinusoidal” pulse shown in column three of Fig. 2 is guessed in this manner. It outperforms the linear sweep by approximately 14%. The “Sinusoidal” protocol in Fig. 2 then becomes the new guess pulse for the optimal control algorithm. After adding more frequency components, RedCRAB obtains the “Optimal (Sin.)” pulse. It outperforms all other pulses in both final polarization (approximately 28% higher with respect to the linear sweep for the short build-up measurement) and polarization rate on our setup.

When the pulse is significantly detuned from the resonance, as in the first 5 µs, the energy gap between the spins is large and so very little polarization can be transferred. As this gap closes, the nuclei are more likely to be polarized and the pulse slows down to allow for an extended transfer period. The detuning “slow down” was recreated with an analytical polynomial function. (For details, see supplementary information. [51]) The resulting “OC fit” pulse largely retains the polarization capability of the optimized pulse. The comparable efficiency corroborates that the “slow down”-feature contributes to the substantial polarization build-up during the first 30 µs. This behavior is reminiscent of optimal adiabatic passages with Landau-Zener protocols and optimal controlled crossings of quantum phase transitions. Both have been investigated in different theoretical and experimental scenarios [54–58] providing a basis for further exploration.

The key result of the paper is shown in Fig. 3, where the RedCRAB-optimized “Optimal (Sin.)” demonstrates two clear improvements over the linear sweep. Firstly, the magnitude of polarization increases by 26% when using the optimized pulse. Secondly, the optimized pulse reaches, in only 3.35 hours, the same polarization that the linear sweep approach obtains after 9 hours of continuously repeating the protocol, making it a factor of 2.6 faster. These times correspond to 98% of the maximum polarization of the linear sweep, which is within the error margin of the polarization measurements. This allows for more than doubling the number of polarized crystals in a given time. Previously, crystals were left to polarize overnight to reach sufficiently high polarization. Using the optimal protocol, it is now possible, on the current experimental setup, to polarize several crystals per day. Due to its increased performance, the “Optimal (Sin.)” pulse was also applied as the hyperpolarization method of choice by Eichhorn et al. [15]. In that paper, a bulk crystal polarization of 25% is achieved using the optimized pulse.

The saturation of the polarization at this higher level is likely due to an equilibrium being reached between the polarizing sequence and the competing $T_1$ decay process of the nuclear spins [17]. The lifetime of the nuclear states is measured to be approximately 3-4 hours under laser illumination, considering the specific values for the magnetic field $B_0$ and temperature. In this case, it is limited due to the laser illumination and MW fields causing, for example, additional heating. While this is the limit for the lifetime during polarization transfer, the polarization can be stored in the sample afterwards for much longer. Lifetimes between 50 hours [15] and 800 hours [12] have been reported for similar crystals at different temperatures and magnetic fields.

II.3. ARISE

Generalizing the steps taken to achieve the results of the previous section, the Autonomous-optimized Repeated Linear Sweep (ARISE) procedure is introduced. Each step provides a recipe for finding a good initial guess for the following optimization. While this should be unimportant for an infinite-dimensionally parameterized optimization without limits and infinite measurement precision, in practice those restrictions apply, leading the algorithm to local instead of global optima. Despite the dCRAB algorithm’s approach allowing it to escape local minima under certain circumstances, the optimization time is also drastically reduced if the initial guess is chosen carefully [32]. The protocol consists of three steps:

1. **Tune the linear sweep.** Do a parameter search for the sweep range $\Delta_{\text{max}}$ and duration $t_{\text{Linear}}$ producing the most efficient polarization transfer.

2. **Construct multi-sweep.** Set up a protocol which sweeps the detuning repeatedly between $\pm \Delta_{\text{max}}$ for $N_{\text{osc}}$ times with a period $\tau$. Do a parameter search for $N_{\text{osc}}$ and $\tau$, starting from $\tau = t_{\text{Linear}}$. 
3. **Apply quantum optimal control.** Search the full function space of the detuning $\Delta(t)$ using an optimal control algorithm. The initial guess is provided by the multi-sweep protocol from the previous step.

In this work, steps one and two are accomplished through a simple parameter sweep. During the second step, the detuning is swept with the function $-\Delta_{\text{max}} \cos(2\pi t/\tau)$, however this could be replaced by linear sweeps. As the setup requires the pulse phase $\varphi_{\text{ext}}(t)$ as an input, all detunings are translated to phase modulations (see Section IV.3). In general, experimental feedback determines the best solution for the respective step. Here, it took the form of the proton NMR signal after 30,000 repetitions of the sequence. The third step is implemented using the RedCRAB software, which suggests different shapes for the phase of the pulse (see Section IV.2).

II.4. **Comparison to simulation**

As shown in tile b of Fig. 1 the electron spin of the pentacene molecule is excited to the $S_1$ state with a short laser pulse. From there it decays to the triplet states $T_2$ and subsequently $T_1$ via ISC [50]. $T_1$ then couples to the nuclear spins in the vicinity of the molecule. The three states of the triplet correspond to spin quantum numbers $m_s = 0$ and $m_s = \pm 1$. An external magnetic field induces a Zeeman splitting of the $m_s = \pm 1$ levels, allowing for a two-level approximation. As the pentacene is deuterated, the resonances of the pentacene’s own nuclear spins are shifted far enough from the other protons in the crystal that they can be neglected. The electron spin is assumed to have its origin at the center of the pentacene molecule. To extract the parallel and perpendicular dipolar coupling to the pentacene’s electron spin, 574 protons of the nearest naphthalene molecules contained in the $3 \times 3 \times 3$ unit cells around the pentacene molecule are modelled (for details, see Section IV.3).

The first column of Fig. 2 shows the external linear sweep approach. Here, the polarization is transferred when the system is close to the fulfillment of the Hartmann-Hahn resonance condition. The external amplitude is kept constant while the frequency is swept across the resonance, allowing for polarization transfer. During the experiment, the polarization plateaus at the center of the pulse before continuing to rise in the second half of the pulse. The simulation results contain the same features, however the plateau is shorter and the initial rise is slightly delayed compared to the experimental data. These differences might be caused by the lack of a full analytical model that extends the existing description of the cavity with distortions due to electronics and other components of the setup. It should be noted that polarization plateaus occur in the simulated results across all pulses when the detuning is above the resonance condition. The relative speed-up of the polarization transfer in the “Optimal (Linear)” pulse is visible in both the simulation, and the experiment. However, a divergence between the measured and the simulation arises in the latter part of the pulse. This could be explained by the very fast oscillations in cavity field amplitude, which are not captured in full detail in the simulation, due to the unknown transfer function of the setup’s electronics.

The simulated polarization of both, the “Sinusoidal” and the “Optimal (Sin.)” pulse, match the experimental data closely. Again, the initial step-plateau-step shape of the “Sinusoidal” is reduced after optimization. Almost all the performance gained by optimizing the pulses arise from the behavior during the first 40-50 $\mu$s of the pulse. This is on a similar timescale as the electron’s decay to the singlet state. In the simulation, the polarization of the longer pulses slowly decreases after ca. 80 $\mu$s. This was not seen in the experiment, most likely due to spin diffusion: The large amount of weakly coupled nuclear spins leads to a slow distribution of polarization away from the electron spin. Spin diffusion is expected on a timescale of ca. 100 $\mu$s according to calculations of the dipolar interaction strength between the protons [17].

III. **DISCUSSION**

The use of closed-loop optimal control provides a strategy for improving hyperpolarized NMR signals in complex experimental setups despite the unknown transfer function. A concern often raised about numerically optimized sequences is that they lose generality and only apply to a specific setup or sample. This is not the case for the “Optimal (Sin.)” sequence which, due to its increased efficiency, has been successfully applied on different crystals with varying spin relaxation times across an extended period of time [15]. This is now the gold-standard pulse in the lab.

The combination of a 15% faster polarization rate and a 26% higher polarization level provides a factor of 2.6 reduction in the time taken to polarize crystals to within the margin of error of the previous method. This allows for multiple crystals to be polarized per day to be used in external hyperpolarization experiments [15]. Furthermore, these improvements lead to higher levels of polarization in a shorter time, resulting in an overall polarization within the crystal of about 25% [15]. Such strongly polarized crystals are necessary to transfer polarization to external nuclear spins. By operating under liquid Helium conditions and with improved crystal quality, even higher values are anticipated [13]. Mimicking the features of the optimized pulse by fitting an analytical function to it (as shown in the supplementary material [51]) retains almost all the improved performance. This is a good starting point not only for future optimization, but also for further investigations of the system dynamics.

A key feature of all the sequences that outperform the linear sweep is that they repeatedly sweep through the cavity resonance. This gives the sequences an extra opportunity to transfer polarization, suggesting that the first sweep leaves some electron polarization untransferred. The simulation shows that the first sweep primar-
illy transfers to one of the most strongly coupled nuclear spins, while subsequent sweeps redistribute the polarization to a wider range of couplings. This type of dynamics can only be accounted for when multiple nuclear spins are considered or the optimization is done on a macroscopic system.

The ARISE protocol offers a starting point for future optimizations of DNP sequences using both open and closed-loop protocols. Inherently flexible, the protocol is easily customized to fit any number of experiment setups, including the complex molecular environment seen here. In conclusion, the application of the ARISE protocol results in a 26% improvement of the polarization level and 15% faster polarization rate. Consequently, crystals were efficiently polarized to 25% bulk proton polarization. These crystals were then used as the polarization source for an external hyperpolarization experiment [15] which demonstrated strong transfer to external spins.

IV. MATERIALS AND METHODS

IV.1. Measurement Technique

The crystal grown in-house is cleaved along the ab crystallographic plane, and it is mounted into a sample holder oriented along the b crystallographic axis. The sample holder is then attached to a motorized stage, enabling it to be shuttled into the MW cavity, where it is cooled to 130 K. Optically Detected Magnetic Resonance (ODMR) can be observed in pentacene-doped naphthalene crystals, where the triplet state is created using a 556 nm laser pulse. By observing the fluorescence of the crystal under constant MW illumination, while changing the magnetic field, the electron spin resonance of pentacene can be found. The high-field transition of the pentacene triplet is used for both alignment and polarization. The crystal is then aligned by monitoring the ODMR spectrum while the sample is rotated, the best alignment is found when the resonance field is maximized. Rabi oscillations are observed with a maximum Rabi frequency of 19.3 MHz, by varying the duration of a resonant MW pulse.

The experimental sequence used to hyperpolarize the sample is shown in Fig. 1 (d). Initially, the sample is shuttled into the MW cavity and a laser pulse is used to create a photo-excited triplet state. A pre-sampled waveform is applied, which has been suggested by the optimal control algorithm, and uploaded to the AWG. To measure the signal produced by the suggested pulse, the sample is shuttled into an NMR coil. Using a Kea NMR spectrometer, the proton polarization is then measured using a single pulse NMR experiment. Integrating over the peak of the resulting NMR spectrum provides a relative estimate of the proton polarization. The RedCRAB algorithm is fed with this integrated signal and its estimated uncertainty to produce the next guess pulse. One experimental cycle lasted approximately 40 seconds, and the optimizations typically ran for 12 hours.

IV.2. Optimal Control

As previously mentioned, methods based on optimal control theory aim to optimize a functional $f$ by modifying time-dependent control functions $u_i(t)$. This functional is the FoM, it includes all the relevant information contributing to the quality of an operation. To simplify the optimization problem, the controls can be parameterized in terms of $N_{be}$ basis functions $v_{i}(t)$ with corresponding parameters $c_{i}$

$$u_{i}(t) = \sum_{\ell=1}^{N_{be}} c_{\ell} v_{\ell}(t). \tag{1}$$

The FoM therefore depends on the coefficients of these basis functions

$$\text{FoM}(u_{i}) = f(c_{i}, v_{i}, t). \tag{2}$$

The solution to the problem is found using an iterative optimization algorithm, which takes in the FoM for a defined set of parameters and returns a new set of parameters. Closed-loop control involves the algorithm directly interacting with the experimental setup. Hence, it automatically takes into account real-world imperfections. Specifics of the measurement technique can be found in Section IV.1. The algorithm improves the FoM by comparing the results from different iterations. It follows the direction of improvement, while exploring the parameter landscape and exploiting its features. An optimal set of controls is eventually obtained after a number of iterations and FoM evaluations.

Limiting the size of the parameter landscape reduces the number of experimental runs and hence the total optimization time. The dCRAB algorithm [32, 38, 39, 59],
in combination with the Nelder-Mead [60, 61] simplex optimization algorithm, is a good choice for this. A small parameter space is created by randomly picking a number of basis functions, optimizing them, and then switching to a new parameter space. An optimization in a single parameter space is called a super-iteration. This allows the optimization to start afresh and continue, even if it temporarily gets stuck in a local optimum.

For the parameterization the Fourier basis is chosen, which provides a simple method to restrict the bandwidth of the controls by limiting their maximum oscillation frequency component through a capping of \( \omega_{d,t} \) in

\[
u(t) = \sum_{d=1}^{N_{de}} \sum_{\ell=1}^{N_{be}} \left[ A_{d,t}^{\text{opt}} \sin(\omega_{d,t}) + B_{d,t}^{\text{opt}} \cos(\omega_{d,t}) \right].
\]

\( N_{be} \) represents the number of basis elements (i.e., the size of the parameter space in each super-iteration), while \( N_{de} \) corresponds to the number of super-iterations. The parameter space of the optimization is spanned by \( c_{d,t} = \{ A_{d,t}^{\text{opt}}, B_{d,t}^{\text{opt}} \} \) while \( \omega_{d,t} \) is randomly initialized with frequencies within a pre-defined interval for each super-iteration defining the basis functions \( v_{d,t} = \{ \sin(\omega_{d,t}), \cos(\omega_{d,t}) \} \). Meanwhile, the length of the pulses is kept constant.

The combination of this limited search space for efficient closed-loop optimization together with the three-step ARISE protocol (see Section II.3) enables the encoding of a sufficient amount of information in the control pulse to substantially increase its performance [62].

### IV.3. System Model

The model for the simulation consists of an electron spin coupled to three nuclear spins. Both the electron and nuclear spins are considered to be spin-half particles. A strong, constant magnetic field \( B_0 = B_0 \hat{z} \) is aligned along the long axis of the pentacene molecule, representing the \( z \)-axis. The total spin Hamiltonian of the electron can be written as

\[
H_{el} = \frac{\hbar}{2} \omega_{0S} \sigma_z + \frac{\hbar^2}{4} D \left( \sigma_z^2 - \frac{1}{3} \sigma_z \right) + E \sigma_z^2 - \frac{1}{9},
\]

where \( \sigma = \{ \sigma_x, \sigma_y, \sigma_z \} \) are the Pauli matrices \( \sigma_z \). The Zeeman interaction is described by \( \omega_{0S} = -\gamma_S B_0 \), where \( \gamma_S \) is the electron spin’s gyromagnetic ratio. The factors \( D \) and \( E \) correspond to the zero-field splitting [50, 63]. The exact transition frequency is determined experimentally, and the magnetic field is aligned such that the splitting is symmetric.

The driving field has a carrier frequency which is resonant with the electron spin \( \omega_{\text{res}} = D - \omega_{0S} \). Its amplitude \( \Omega_{\text{ext}}(t) \) and phase \( \varphi_{\text{ext}}(t) \) are modulated to control the system. It is then transformed to the field inside the cavity \( \Omega_{\text{int}} \) using Eq. (9). Coupling between the electron and nuclear spins is described by the hyperfine interaction tensor \( A^i \) with the nuclear spin indices \( i = \{ 1, 2, 3 \} \). A detuning \( \Delta_{es} \) is introduced, describing the deviation of the field inside the cavity from the electron resonance frequency. In the rotating frame of the MW, applying the rotating wave approximation, the Hamiltonian is then given by [64]

\[
H = \hbar \left( \text{Re}[\Omega_{\text{int}}(t)] S_x + \text{Im}[\Omega_{\text{int}}(t)] S_y + \Delta_{es} S_z \right)
\]

\[+ \omega_1 \sum_{j=1}^{3} I_z^j + \sum_{i=1}^{3} S \cdot A^i \cdot I^i),\]

where \( S = \{ S_x, S_y, S_z \} \) with \( S_k = \frac{1}{2} \sigma_k \otimes 1 \otimes 1 \otimes 1 \), \( k \in \{ x, y, z \} \) are the electron’s spin operators. \( I^j \) and \( I_z^j \) are the equivalent operators for the nuclear spin with index \( i \) and \( \Omega_{\text{int}} \) is the complex, time-dependent field inside the cavity \( \omega_L \approx 9.2 \text{MHz} \) corresponds to the Larmor frequency of the nuclei. The voltage signal, which is fed into the AWG, is given by

\[
V_{\text{ext}} = V(t) \cos \left( \omega_{\text{res}} + \Delta_{es} t + \varphi_{\text{ext}}(t) \right).
\]

The conversion between \( V(t) \) and \( \Omega_{\text{ext}}(t) \) is determined directly from experimental data. The phase modulation \( \varphi_{\text{ext}}(t) \) can be translated into the drive detuning \( \Delta(t) = \tilde{\varphi}_{\text{ext}}(t) \).

In the secular approximation [65], only the dominant coupling terms along \( z \) are kept, giving

\[
S \cdot A^i \cdot I^i = S_z \cdot \left( A_x^i I_x^i + A_y^i I_y^i + A_z^i I_z^i \right).
\]

They are calculated for the respective position of the nucleus in the crystal structure by considering a purely dipolar interaction [66].

The static detuning values \( \Delta_{es} \) for the Hamiltonian shown in Eq. (5) are drawn from a normal distribution with a full width half maximum (FWHM) of 10 MHz to mimic additional frequency shifts due to magnetic field inhomogeneities and other impurities.

The system description includes the dephasing of the electron spin via a Lindblad operator \( R_1 = \sqrt{\Gamma_{\text{el}}} S_z \), where \( \Gamma_{\text{el}} \) is the dephasing rate [67]. The only electron states that interact with surrounding nuclei are the \( |0 \rangle \) and \( |1 \rangle \) states in the \( T_2 \) triplet (see Fig. 1). To account for the decay from \( T_2 \) to \( S_0 \), the model includes a shelf state, which does not interact with the drive. It is only coupled via the loss rates \( \Gamma_{\text{loss},0} \) and \( \Gamma_{\text{loss},1} \) from the respective triplet states. The corresponding Lindbladians are given by \( R_2 = \sqrt{\Gamma_{\text{loss},0}} |s \rangle \langle 0 | \) and \( R_3 = \sqrt{\Gamma_{\text{loss},1}} |s \rangle \langle 1 | \) with \( |s \rangle = |s \rangle \langle 0 | \) and \( |s \rangle = |s \rangle \langle 1 | \).

The evolution of the density matrix is then solved using the Lindblad master equation

\[
\dot{\rho} = -\frac{\imath}{\hbar} [H, \rho] + \sum_{j=1,2,3} \left( R_j \rho R_j^\dagger - \frac{1}{2} R_j^\dagger R_j \rho - \frac{1}{2} \rho R_j^\dagger R_j \right),
\]

where \( \rho \) is the density matrix of the system.
ΔI(γ) = \int \frac{dΩ}{dΔcs}ΔI

FIG. 5. Characterization of the set-up via response factor γ. The agreement between experiment and simulation, ΔI, is calculated via the Fourier transform Ω of the driven Rabi signal for varying cavity detunings (top). The integral indicates the overlap of measured and simulated distribution, which is shown for different values of cavity response fed to the simulation in the bottom plot. The black line indicates the minimum of the error in overlap between simulation end experiment at γ_{cav} = 9.24 MHz (bottom).

The effect of the cavity on the external driving field is characterized by the cavity response factor γ_{cav} and given by the differential equation

\frac{∂}{∂t} \Omega_{int}(t) = γ_{cav} \left( Ω_{ext}(t) \cdot e^{-iϕ_{cav}(t)} - Ω_{int}(t) \right) - iΔcsΩ_{int}, \tag{9}

where Δcs describes the constant detuning of the cavity from the resonance of the electron spin transition frequency [68].

The solutions to the differential equations in Eq. (8) and Eq. (9) are calculated numerically using the DifferentialEquations.jl [69] and other Julia packages [70–84]. To obtain a realistic polarization build-up in Fig. 3, Eq. (8) is solved for and averaged over 1000 instances. For each instance, three random but distinct nuclei are picked from the 30 most strongly coupled nuclei and the detuning Δcs is sampled from a Gaussian distribution. This way, mechanisms which are neglected in the common weighted sum single nucleus approximation are captured. Examples include the re-polarization of the electron spin through partially polarized nuclei or the redistribution of polarization from one nucleus to another. The mean over many runs with different coupling combinations takes into account the variety of couplings in the system with reasonable computational resources.

The cavity response γ_{cav} is determined by repeatedly applying constant external drive fields with different cavity detunings Δcs, obtaining a photon count that corresponds to the electron state. \( B_0 \) is adjusted such that the spin always stays resonant with the drive frequency. Oscillations are recorded for times up to 0.6 µs from the start of the drive pulse. The detuning is swept through a range of ±25 MHz around the resonance. The maximum of the Fourier transform of the photon count then corresponds to the Rabi frequency Ω for a detuning Δcs. The cavity dynamics are complex, leading to a response similar to the example shown at the top right of Fig. 5. These measurements are modeled for an electron spin inside a cavity with a response factor γ_{cav} between 5 and 14 MHz (range suggested by response time based on the measured Q factor of the resonator using a spectrum analyzer). The resulting Fourier transforms are compared to the experimental values. The comparison was done by calculating the overlap of the normalized measurement and simulation grids as shown in Fig. 5. The minimum of the sum of the absolute difference between each grid point of the measurement and simulation data is obtained by a Gaussian fit resulting in γ_{cav} = 9.24 MHz.

The values for the decoherence rate, \( Γ_{el} \), of the electron spin and the loss rates to the shelf state, \( Γ_{loss,0} \) and \( Γ_{loss,-1} \), are found by performing a Hahn echo measurement and state-dependent lifetime measurements. For the dephasing time of the electron we obtain 1/\( Γ_{el} \) = 10 µs and the triplet-state decay times are measured to be 1/\( Γ_{loss,0} \) = 80 µs and 1/\( Γ_{loss,-1} \) = 180 µs.

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AUTHOR CONTRIBUTIONS

AM and CM performed the experiments with help of JS, and PN. TR simulated the system with support from PR, AM, and MMM. TR, PR, and MMM developed the theoretical model and facilitated access to, maintained, and tailored the closed-loop control software. AM and CM integrated and configured the control software to work with the experiment. MG grew the sample, while TE provided background on the properties and structure of pentacene-doped naphthalene. JMS and PH provided help with the implementation of the ISE-like linear sweep and advice on growing the pentacene-naphthalene crystals. The setup was characterized by AM, TR, PR, CM, and JS. The original project was planned by PN, together with SM, AM, and PR. AM, TR, PR, CM, JS, MMM, and PN discussed, and analyzed the results. PN, MMM, IS, SM, MBP, FJ, and TC supervised the project. All authors contributed to the manuscript.
COMPETING INTERESTS

The authors declare no competing interests.

DATA AVAILABILITY

All data that support the plots within this paper and other findings of this study are available from the corresponding authors upon reasonable request.

CODE AVAILABILITY

All code that support the plots within this paper and other findings of this study are available from the corresponding authors upon reasonable request.

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Supplementary Material: Macroscopic Hyperpolarization Enhanced with Quantum Optimal Control

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I. AMPLITUDE VS. PHASE VARIATION

Figure 1. Amplitude vs phase variations: Comparing the linear sweep (Linear) to the corresponding QOC-generated pulse (Optimal (Linear)), as well as combinations of both. In the third and fourth column the amplitude array of one is combined with the phase array of the other (Optimal amplitude + Linear phase and Linear amplitude + Optimal phase). The increase in polarization over the optimization is caused solely by the changes in phase rather than amplitude (compare highlighted plots).

To separate the respective effects of amplitude and phase modulation these two parameters are investigated independently (Fig. 1). We first ran the basic linear sweep and the Optimal (Linear) pulse, where we saw that the optimized pulse leads to higher polarization. To test only the optimized amplitude modulation the optimized phase is reset to

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the initial guess while the phase modulation was kept (Optimal amplitude + Linear phase). Similarly, to test the optimized phase modulation the amplitude is held constant, as in the linear sweep, and the optimized phase is applied (Linear amplitude + Optimal phase).

By comparing those four pulses it becomes clear that the amplitude modulation plays no role in the polarization transfer and only the pulses with optimally controlled phase modulation lead to enhanced polarization (highlighted in Fig. 1). Testing the phase of the optimized pulses with different constant MW amplitudes shows that using a higher MW amplitude always leads to better polarization transfer (see Fig. 3).

II. SINE OSCILLATION FREQUENCY TESTS

Figure 2. Comparing different sinusoidal pulses. Upper left: Half oscillations width different frequencies comparable to different speeds of the ISE-like linear sequences. Upper right: Example pulses to visualize the idea of the measurement. Lower left: For all six frequencies of the first plot we measure the polarization after up to eight half oscillations and compare it to the polarization after the linear sweep (dashed line). Lower right: Sinusoidal pulse that gave the highest polarization.

Following the idea that subsequent sweeps through the resonance in alternating directions further enhance the polarization, we tried to polarize with a sinusoidal pulse. In order to find the optimal pulse, we were varying both, the frequency of the oscillation and the number of resonance passages. For better comparison we here use the length of a half oscillation as a parameter instead of the frequency, which means passing through the resonance once, similar to a basic ISE-like linear sweep (Fig. 2, upper left). The second parameter, that describes the passages through the resonance is then given by the number of half oscillations (examples given in Fig. 2, upper right).

In (Fig. 2, lower left) we compare the polarization that we got for different parameter sets (length and number of half oscillation) to the standard linear sweep (dashed line). We find that increasing the number of resonance passages leads to an increase in polarization for a lengths. While most of the applied pulses are beating the standard linear pulse we found maximum polarization for a length of 20 μs and 8 half oscillations (Fig. 2, lower right). This pulse was characterized in the main text and used a a new starting point for the sinusoidal based optimal control.
III. OC FITTED PULSE

The “OC fit” pulse shown on the right-hand side in Fig. 3 was designed by modelling the shoulder feature of the sin.-based OC pulse resulting from closed-loop optimizations of the sinusoidally varying pulse in the detuning regime. Repeating mirrored polynomial functions emulate the slow-down of the detuning sweep around resonance. A variation of the externally applied voltage kept constant during the pulses displays an improvement of polarization transfer for higher external drive amplitude. Except for the highest driving amplitudes, at the limit of the experimental capabilities, the fitted pulse is equal or outperforms the pulse resulting from the closed-loop iterations. Therefore it serves as a good starting point for the use in other, similar setups and further optimisations as well as theoretical and analytical transfer calculations and numerical simulations.

IV. NAÏVE SWEEP CORRECTIONS

While we applied a linear sweep outside the cavity, the mentioned effects lead to a non-linear sweep inside the cavity. However, the drive would be faster when passing the cavity resonance, compared to the part of the sweep where we are outside of the cavity. Measuring the cavity linewidth and Q-factor allows to calculate the expected deviation from the linear sweep. Calculating an input function with modified amplitude that takes the cavity properties into account would be the first na¨ ıve approach to overcome this issue. Trying this did however not improve our polarisation values.

V. COHERENCE MEASUREMENTS

We measured the nuclear spin relaxation time $T_1$ and the electron spin coherence time $T_2$. For the nuclear spins, we measured $T_1$ under experimental conditions (e.g. temperature, laser illumination) and got a value of around
For the $T_2$ coherence time of the electron spin, a standard Hahn-Echo sequence [1] was used and a value of around $9\,\mu$s was obtained. (Fig. 4 right).

Figure 4. Left: $T_1$ measurement of the nuclear spins under experimental conditions. Right: $T_2$ measurement of the electron spin via Hahn-Echo.

VI. POLARIZATION BUILD-UP

We can build up polarization $p$ in the crystal iteratively by applying the basic polarization sequence many times (see Fig. 3 in the main text). The final polarization will be given at the equilibrium of two competing effects: each time we apply the basic sequence a fraction $\alpha(1-p)$ of the remaining unpolarized nuclear spins will be polarized, where $\alpha$ is the polarization power of the sequence. At the same time, the polarized nuclear spins decay at a constant rate $\gamma$.

\[
\frac{dp}{dt} = \alpha(1-p) - \gamma p
\]  

(1)

Solving leads to the equation

\[
p(t) = p_{\text{max}} \left(1 - e^{-\tilde{\gamma} t}\right),
\]

(2)

where $p_{\text{max}} = \alpha/(\gamma + \alpha)$ and the parameter $\tilde{\gamma} = \gamma + \alpha$ can be obtained from a fit to the data. We obtain $\tilde{\gamma} \approx 0.0061\,\text{min}^{-1}$ and $p_{\text{max}} \approx 14140\,\text{a.u.}$ from the polarization build up obtained by the linear sweep and $\tilde{\gamma} \approx 0.0071$ and $p_{\text{max}} \approx 17850\,\text{a.u.}$ from the polarization build-up obtained from the optimal sequence. An additional measurement $T_1$ measurement gives $1/\gamma \approx 223\,\text{min}$ (Fig. 4 left). This translates into estimates for the final polarization of $p_{\text{max}} \approx 27.8 \pm 1.3\%$ for the linear sweep and $p_{\text{max}} \approx 35.1 \pm 1.7\%$ for the optimal sequence. Note, that the true value of $\gamma$ is probably slightly larger than in the $T_1$ measurement due to the polarization pulse sequences. If we consider, e.g., $1/\gamma \approx 200\,\text{min}$ (or $1/\gamma \approx 180\,\text{min}$), the polarization for the optimal sequence drops to $p_{\text{max}} \approx 26.2 \pm 3.4\%$ (or $p_{\text{max}} \approx 16.5 \pm 5.2\%$) and similarly for the linear sweep.

VII. EFFECT OF THE NUMBER OF NUCLEI ON THE MODEL

Each electron spin is surrounded by a large number of protons forming the nuclear spin bath. As only a limited amount can be simulated at a time, sub-groups of nuclei are considered and averaged over. Fortunately, the molecular and crystallographic properties of the naphthalene-$h_8$ specimen doped with pentacene-$d_{14}$ are well-known. Hence, the orthogonal ($A'_{zx}$, $A'_{zy}$) and parallel ($A'_{zz}$) parts of the hyperfine tensor can be directly calculated [2] for the surrounding protons in the crystal. Instead of including the entire bath as a single effective nuclear spin [3], several nuclei are considered individually in the polarization dynamics. This step is necessary to reflect the effects caused by complex pulse shapes obtained by the optimization as well as the distortion by the cavity. Since the pulses cross the resonance line multiple times and are repeated successively for polarization build-up, strongly coupled nuclei are usually polarized first but can be depolarized again so that excitation is transferred to other nuclear spins. Because the electron spin is re-initialized before each pulse application, each iteration can polarize different nuclei. Up to six nuclei were considered during the initial investigation. However for the figures presented in this manuscript, the following combinations of spins was used to keep computational resources within an acceptable range: The electron spin is coupled to three nuclear spins where the hyperfine coupling values are randomly selected from the top 30 most...
strongly coupled protons. This simulation is repeated and average for 1000 sets using three different random nuclei in each run. This captures the dynamics of multiple protons coupling to the electron at the same time, as well as the repetition of the transfer operation in the experiment.

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