Electron-to-nuclear spectral mapping via dynamic nuclear polarization

Arjun Pillai, Moniish Elanchezhian, Teemu Virtanen, Sophie Conti, and Ashok Ajoy

ABSTRACT

We report on a strategy to indirectly read out the spectrum of an electronic spin via polarization transfer to nuclear spins in its local environment. The nuclear spins are far more abundant and have longer lifetimes, allowing for repeated polarization accumulation in them. Subsequent nuclear interrogation can reveal information about the electronic spectral density of states. We experimentally demonstrate the method by reading out the ESR spectrum of nitrogen vacancy center electrons in diamond via readout of lattice $^{13}$C nuclei. Spin-lock control on the $^{13}$C nuclei yields a significantly enhanced signal-to-noise ratio for the nuclear readout. Spectrally mapped readout presents operational advantages in being background-free and immune to crystal orientation and optical scattering. We harness these advantages to demonstrate applications in underwater magnetometry. The physical basis for the "one-to-many" spectral map is itself intriguing. To uncover its origin, we develop a theoretical model that maps the system dynamics, involving traversal of a cascaded structure of Landau–Zener anti-crossings, to the operation of a tilted "Galton board." This work points to new opportunities for "ESR-via-NMR" in dilute electronic systems and in hybrid electron–nuclear quantum memories and sensors.

I. INTRODUCTION

The central spin model is the physical description underlying a wide class of quantum mechanical systems relevant in quantum information processing, sensing, and dynamic nuclear polarization (DNP). This includes solid-state qubits or sensors constructed out of electronic defects and donors in materials, such as silicon and diamond, and in the context of DNP, radical species embedded within nuclear spins of analytes of interest. These systems are typically comprised of dilute electronic spin centers interacting with a several-fold larger nuclear spin bath [schematically shown in Fig. 1(a)].

The control and readout of such electronic spins form the basis for quantum sensing. Magnetometry with diamond Nitrogen Vacancy (NV) centers leverages the ability of the NV electronic spin to be optically initialized and read out at room temperature. Let $g(B_0, f)$ denote the NV electronic spectrum at bias field $B_0$ and frequency $f$. Optical readout, as in optically detected magnetic resonance (ODMR) maps $g$ to fluorescence contrast $S[g]$ by exploiting the differential optical contrast between the triplet ground state levels $m_s = \{0, 1\}$ originating from state-selective branching in the excited state. Ensemble DC magnetometry then entails measuring a fluorescence change upon a shift in the electronic spectrum $\delta S = S[g(B_0 + \delta B, f)] - S[g(B_0, f)]$ when subject to a probe magnetic field $\delta B$.

Spin-fluorescence mapping, while attractive in many contexts, suffers from technical limitations that can reduce sensitivity in some operational scenarios. A typical example is when the N–V axis is misoriented with respect to $\vec{B}_0$. State mixing in the excited state then leads to a steep drop in fluorescence and ODMR contrast. Even when perfectly aligned, typical fluorescence contrast levels are $\lesssim 5\%$ and susceptible to optical backgrounds and readout laser amplitude noise. In scenarios requiring quantum sensing in fluidic (or optically dense) media, optical scattering can further reduce contrast. There has been broad interest in alternate strategies that map the NV electronic populations into other parameters (e.g., charge) that can be efficiently readout.

Here, we demonstrate an alternate route to reading out the NV electronic spectrum via $^{13}$C nuclear spins in the surrounding...
environment [Fig. 1(a)]. Our strategy relies on mapping the NV spectral density of states (DOS) at frequency \( \text{DOS}(\Delta f) \) into \( ^{13}\text{C} \) nuclear polarization \( P \) [see Fig. 1(b)],

\[
\delta g(B_0, f_0) = \int_{\Delta f/2}^{\Delta f/2} \frac{g(B_0, f) df}{g(B_0, f) df} \rightarrow P,
\]

where \( \rightarrow \) refers to an approximate map in the limit \( \Delta f \to 0 \). The \( ^{13}\text{C} \) nuclei are subsequently inductively readout via RF techniques [nuclear magnetic resonance (NMR)], providing certain natural advantages over optical readout: it is crystal orientation independent, background-free, and immune to fluorescence fluctuations due to scattering.

This "one-to-many" spectral map suggests that "ESR-via-NMR" may be feasible in central spin systems, where a dilute species can be read out through a more abundant spin species coupled to it. This bears similarity to the chemical exchange saturation transfer (CEST)-like quadrupole detection described in Ref. 27. While some aspects of the physics here are easy to intuit—sweeping over a part of the electronic spectrum where there is negligible electronic DOS intensity leads to no hyperpolarization—it is still mysterious that narrow sweeps applied to the wing of a spectral line should produce a \( ^{13}\text{C} \) polarization that seemingly tracks the local spectral DOS. We note, however, that the fact that the DNP enhancement amplitude reflects the underlying electronic spectrum, at least qualitatively, is common knowledge.23,33 It is widely employed in experiments optimizing DNP levels and to characterize the effectiveness of a radical species in yielding hyperpolarization.32 However, in the present work, we seek to make this connection more quantitative, exploiting the DNP levels here to "sense" the ESR spectrum. Ultimately, this also portends applications in magnetometry, exploiting the ability to readout the nuclear spins with high signal-to-noise ratio using spin-locking techniques.

We benefit in this endeavor from special features of the employed DNP mechanism23,35,36 [Fig. 1(c)]. Every part of the spectrum produces hyperpolarization, but of an identical sign. This is in contrast to common DNP techniques (e.g., solid effect) where the DNP sign is inverted at the red or blue shifted side of the spectral center. The latter can cause cancellation in the DNP enhancements between different parts of the spectrum, especially at low fields or for inhomogeneously broadened spectra, making determining the underlying spectrum non-trivial.

It is evident that a full description of the DNP mechanism that results in polarization even when sweeping over the wing of the electronic spectrum should include the physics of polarization dynamics when the electron is coupled to \( N \) nuclear spins. In that respect, in this work, we discuss strategies for the analytic descriptions of DNP in the large \( N \) limit, extending common approaches that focus primarily on \( e-n \) or \( e-e-n \) systems (e.g., solid and cross effects), where larger nuclear networks are evaluated fully numerically.5,36,37 Indeed, previous calculations of the DNP technique35 employed here were also carried out only in the single \( e-e-n \) limit.38 Instead, in this paper, relying on a set of simplifying assumptions, we show that a mechanistic description with \( N \) coupled nuclei as in Fig. 1(a) is tractable and can lead to experimentally verifiable predictions.

II. System

Experiments here are carried out on a single-crystal sample with an ensemble of ~1 ppm NV centers [Fig. 1(a)]. The NV spectrum \( g(B_0, f) \) [red line in Fig. 1(b)] is constructed out of both homogeneous and inhomogeneous contributions: the former primarily due to interactions with lattice \( ^{13}\text{C} \) nuclei and the latter on account of strain and orientational effects.33 Figure 1(b), for instance, describes the spectral DOS \( \delta g \) in window \( \Delta f \) (purple) arising from an NV center hierarchically coupling to multiple \( ^{13}\text{C} \) nuclei.39

Our strategy to map the electronic spectrum \( g \) is outlined in Fig. 1(c). DNP is applied via chirped MWs24 with a bandwidth \( B = \Delta f \) window [Fig. 1(b)] over \( g(B_0, f_0) \) to transfer the corresponding \( \delta g \) information to \( ^{13}\text{C} \) population differences. This typically involves ~10 MHz sweeps [left panel of Fig. 1(c)], during which polarization is accumulated in the \( ^{13}\text{C} \) nuclei. Figure 2 demonstrates that the corresponding \( ^{13}\text{C} \) polarization closely tracks the electronic DOS \( \delta g \) in the \( \Delta f \) window swept [see Fig. 1(b)]. A novelty in this work with respect to previous reports34,40,41 is the enhanced signal-to-noise ratio (SNR) readout of the \( ^{13}\text{C} \) nuclei. We employ a pulsed spin-locking protocol42,43 [right panel of Fig. 1(c)] that allows the \( ^{13}\text{C} \) populations to be continuously interrogated for long periods up to the limit set by the rotating-frame lifetimes, typically \( T_2 > 2 s \).25 It consists of a train of \( \pi \) pulses spin-locked with the initial \( ^{13}\text{C} \) spin state [Fig. 1(c)], simultaneously inhibiting dipolar interactions and \( e \)-induced dephasing. Inductive readout (with bandwidth \( = 10 \text{ kHz} \)) occurs after every pulse [red line in Fig. 1(c); typical experiments...
involve >100 K pulses. This yields a $^{13}$C readout SNR that is boosted by $\geq 10^{3}$ times\footnote{At $B_0 = 33.6$ mT in $\Delta f = 10$ MHz windows (purple) whose middle is denoted by $f_0$ [see Fig. 1(b)]. Red (blue) data correspond to 1% (3%) $^{13}$C-enriched crystals. The four NV families here are aligned at $54^\circ$ to $B_0$ and overlap in frequency. Solid lines are Gaussian fits. Linewidth $\ell$ increases with enrichment. Visible are satellites corresponding to NV centers with first-shell $^{13}$C nuclei. Inset (i) zoomed view of satellites, offset $-99.7$ MHz from the main peak. Normalized spectra show $\equiv 2.75$ greater satellite intensity for the 3% enriched sample. (b) Linewidth $\ell$ of a $^{13}$C-mapped NV spectral peak for a single NV center family for different $\Delta f$ window widths. Error bars are calculated from Gaussian fits. The solid line is a spline-fit guide to the eye. Linewidths $\ell$ grow with window size $\Delta f$ and saturate at $\ell = 2$ MHz for $\Delta f < 1$ MHz. (c) Log scale representation of data for 1% enriched sample from (a). Solid lines are Gaussian fits. Satellites are $\equiv 0.02$ the intensity of the main peak. (d) DNP buildup curves, showing $^{13}$C polarization buildup for different points (i)–(vi) labeled in (f). Solid lines are biexponential fits. (e) DNP buildup in the small-time limit is approximately linear (solid lines), (f) Extracted buildup rates (colored points (i)–(vi)) from the linear fits in (e) with error bars. These rates closely overlay the NV spectrum (lighter purple points), obtained similar to (a). (g) Measured $^{13}$C relaxation times for different spectral locations $\ell$ (i)–(vi) in (d)–(f), demonstrating that relaxation rates are constant ($\equiv 30$ s$^{-1}$). (h) $^{13}$C-mapped NV spectra obtained under alternate MW sweep directions with $\Delta f = 3$ MHz. Data here are on a single NV center family. Signal intensities are sweep-sign dependent, but otherwise identical for the entire spectrum.

III. NV $\rightarrow^{13}$C SPECTRAL MAP

Figure 2 elucidates results of spectral mapping. In Fig. 2(a), we consider two single crystal samples with $^{13}$C enrichment levels at 1% (red) and 3% (blue), respectively. Points here denote the single-shot inductively detected $^{13}$C signal intensity at 7 T following Fig. 1(c) with $\Delta f = 10$ MHz (purple window). The high SNR data trace the underlying NV electronic DOS $\delta g(B_0, f)$ with excellent fidelity (solid lines are Gaussian fits), reflecting that the map in Eq. (1) is, indeed, viable. For instance, there is no measurable $^{13}$C signal (within noise) for $f_0$ where the NV spectral DOS is zero. Intriguingly, however, for a $\Delta f$ window even in the wing of the spectrum (purple window in Fig. 1(b)), the $^{13}$C signal reflects $\delta g$.

We observe two satellites, offset at $-99.7$ MHz from the spectral center [zoomed in Fig. 2(a-i)]. We identify them as arising from NV centers possessing a $^{13}$C nucleus in the first shell;\footnote{One can unravel $\delta g$ information via polarization funneled into them from NV-proximal nuclei.} the high SNR $^{13}$C readout here allows them to be easily discerned despite their low concentration ($\approx 3\%$ of all NV centers in the 1% enriched sample). Figure 2(a-i) shows that while we probe only bulk $^{13}$C nuclei (hyperfine shifted by $< 10$ kHz), one can unravel $\delta g$ information via polarization funneled into them from NV-proximal nuclei. Figure 2(c) shows data for the 1% enriched sample in a logarithmic scale; the ratio of the satellite and main peak intensities ($\equiv 0.02$) approximately follows the expected 3.3% concentration. Returning to Fig. 2(a), it is evident that increasing $^{13}$C enrichment yields a larger electronic spectral broadening\footnote{For example, for a $\Delta f$ window in the wing of the spectrum (purple window in Fig. 1(b)) the $^{13}$C signal reflects $\delta g$.} and increased (relative) satellite intensity, both as theoretically predicted. Figure 2(b) describes the measured spectral linewidth $\ell$ [arrows in Fig. 2(a)] as a function of the sweep window $\Delta f$ employed. It increases approximately linearly with $\Delta f$, as expected from Eq. (1), and saturates at $\ell = 2$ MHz, which correlates with the linewidth due to strain-broadening.\footnote{Error bars here are obtained from the Gaussian fits.}
Some key features of the spectra in Fig. 2(a) are worth mentioning. Here, the NV center families have their NV axes at $54^\circ$ to the bias field $B_0$; a regime of strong misorientation where ODMR suffers significant ($\geq70\%$) contrast loss.\textsuperscript{23,24} RF readout here is background free, and spin-locking provides a significantly higher SNR compared to previous reports.\textsuperscript{23,25,26,29} As opposed to solid-effect DNP\textsuperscript{22,23} or that obtained at the NV excited state anti-crossing (ESLAC),\textsuperscript{33,34} the sign of the $^{13}$C NMR signals obtained via Fig. 1(c) is identical for the entire spectrum in Fig. 2(a).\textsuperscript{42} This makes unraveling the electronic spectra feasible even when they are inhomogeneously broadened (see Fig. 3).  

What is the physical origin of a higher $^{13}$C polarization for a spectral point $f_j$ at the peak in Fig. 2(a) vs at the wing? An insight is provided in Figs. 2(d) and 2(e), which consider how the growth of nuclear polarization relates to the electronic DOS. We study polarization buildup curves for representative points $f_j$ on the spectrum $g(B_0, f_j)$ (marked (i)–(vi) in Fig. 2(f)) for the natural abundance (1%) sample. The points in Fig. 2(a) reflect a slice of these data at $t = 20$ s. Polarization buildup reflects an interplay between spin injection into directly hyperfine coupled $^{13}$C nuclei, spin diffusion, and $^{13}$C relaxation. To a good approximation, $^{13}$C relaxation rates are determined by interactions with paramagnetic impurities (P centers)\textsuperscript{33,34,43} and are independent of the spectral location $f_j$ being probed. This is shown in Fig. 2(g), where we find $T_{1N} \approx 30$ s (dashed line) independent of $f_j$ (see the supplementary material). Similarly, spin diffusion rates, driven by internuclear interactions, can be considered to be independent of $f_j$.\textsuperscript{44} One expects then that data in Fig. 2(a) arise from differences in polarization injection rates conditioned on $f_j$; this, in turn, produces the frequency-dependent polarization levels and yields Eq. (1). Experiments in Figs. 2(d)–2(f) confirm this intuition. We restrict attention to short-time ($<1$ s) buildup [zoomed in Fig. 2(e)] and linearize the corresponding polarization growth curves (solid lines) to extract the injection rate. Normalizing and overlaying these values (colored points) on the normalized $^{13}$C-interrogated NV electronic spectra in Fig. 2(f) (lighter purple points) show that the polarization injection rates produce the signal differences that track $\delta g(B_0, f_j)$.  

Finally, Fig. 2(h) illustrates the result of an experiment similar to Fig. 2(a) (with $\Delta f = 3$ MHz), but focused on a single NV center family and employing alternate MW sweep conditions (low-to-high or high-to-low frequency). Both cases in Fig. 2(h) reflect the electronic spectrum, but with an opposite sign. There is a small observable shift ($\approx2.3$ MHz) from the spectral center.

IV. EXPERIMENTAL OUTLOOK

Figure 2(a) suggests the possibility to perform “ESR-via-NMR,” portending avenues to probe electronic spins via nuclei coupled to them. We envision applications in systems beyond NV centers in diamond where it would be useful to extract the ESR spectra of dilute radicals embedded in a nuclear environment, such as endogenous radicals and active sites (for instance, in photosynthetic complexes) or photopolarizable radicals.\textsuperscript{37} In such systems, ESR spectra may be inaccessible, and it would be useful if information were, instead, relayed to more abundant, longer-lived nuclear spins to be read out. Such “one-to-many” spectral maps also suggest applications in quantum memories.\textsuperscript{45}

From a technological perspective, we envision applications in RF ($^{13}$C) interrogated NV-center magnetometry without the use of a MW cavity.\textsuperscript{23,44} As opposed to optical NV sensors, this can permit DC magnetometers that function in turbid or scattering media and with arbitrarily oriented crystals. Figure 3 demonstrates a proof-of-concept, employing NV $\rightarrow ^{13}$C maps for bulk DC magnetometry underwater, a regime with several applications (e.g., undersea magnetic anomaly detection\textsuperscript{38}), but where current quantum sensor technologies are not viable. Figures 3(a) and 3(b) show NV spectra for samples placed under $\approx4.9$ ml of water, corresponding to about 2000-fold the volume of the sample. Here, the four NV axes are identically aligned at $54^\circ$ to the bias field [Fig. 3(a)] and arbitrarily oriented [Fig. 3(b)]. We clarify that only the sample (and not the excitation and detection apparatus) is submerged, but these experiments suggest that fully underwater quantum sensor magnetometers are feasible.

DC magnetometry can be carried out by monitoring the NV spectral shift under an applied probe field $B$. Figures 3(c) and 3(d) show the resulting individual $^{13}$C-interrogated spectra, from where we estimate an underwater DC sensitivity $\approx363 \text{ nT/}\sqrt{\text{Hz}}$. Sensitivity is governed by the NMR readout SNR, which is still limited here due to the relatively low NMR coil filling-factor ($\approx0.004$), $^{13}$C hyperpolarization level ($\approx0.2\%$), and small readout time (0.3 s) with respect to the dead-time. These factors can be considerably improved with advancements to the experimental apparatus (see Ref. 25); we estimate that a sensitivity improvement by four orders of magnitude is feasible. Overall, we imagine applications in systems where the high abundance and long $T_2^*$ lifetimes of the nuclear spins being probed will compensate for losses stemming
from the low $\gamma_e/\gamma_n$ ratio (here, $\gamma_e$ and $\gamma_n$ refer to the nuclear and electronic gyromagnetic ratios, respectively). Figure 3(b) also suggests underwater vector magnetometry exploiting the four NV center families simultaneously.26

V. MECHANISTIC DESCRIPTION OF HYPERPOLARIZATION

Experiments in Figs. 2 and 3 give rise to the intriguing question: why is the map in Eq. (1), even if just approximate, possible at all? This can be recast to asking why DNP in a MW sweep in the wing of the spectrum [as in the purple window in Fig. 2(a)] should produce a signal tracking $\Delta$. Quantitatively modeling polarization transfer at the spectral wing requires the ability to solve $\delta$ at all? This can be recast to asking why DNP in a wing of the spectrum [as in the purple window in Fig. 2(a)] produces a map in Eq. (1), even if just approximate, possible at all? This can be recast to asking why DNP in a wing of the spectrum [as in the purple window in Fig. 2(a)] produces a map in Eq. (1), even if just approximate, possible at all?

Here, we develop an approach to make such solutions tractable at large $N$. Appendices A–D elucidate this theory in greater detail; here, we present its salient aspects and connections to experiments.

The instantaneous Hamiltonian of the $e-n$ system at a particular frequency $f_M W(t) = B f t + f_0 - B/2$ [Fig. 1(c)] along the MW sweep is

$$\mathcal{H}(\omega_M) = (\Delta - \omega_M) S_z^2 + \gamma_e B_0 S_z + \Omega_e S_x + \sum_{j=1}^N \omega_j^{(0)} P_0 I_{2j} + \omega_j^{(1)} P_1 I_{2j'},$$

where we restrict attention to the $m_s = \{0, +1\}$ manifold and ignore internuclear interactions and where $\omega_M = 2\pi f_M$, $\Delta = 2.87$ GHz is the NV center zero field splitting, $\Omega_e$ is the electronic Rabi frequency, and $P_0 = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$, $P_1 = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$ are projection operators (see Appendix B 2). The eigenenergies of $\mathcal{H}(\omega_M)$ manifest as a cascade of Landau–Zener (LZ)-LACs, the number of which scale exponentially with $N$. Figure 4(a) shows this for a representative example of $N = 3$ and positive hyperfine couplings $A > 0$.

Modeling experiments in Fig. 2(a) requires a machinery to track the nuclear populations as this LZ cascade is traversed. We first extract the 2$^N$ LAC points to a 2D checkerboard $T_{LZ}$ [Fig. 4(b)] of

---

**FIG. 4.** “Galton board” nuclear hyperpolarization and DOS mapping. (a) LZ anti-crossings (LZ-LACs). For $N = 3$, lab frame energy levels of Fig. 1(b) manifest in the rotating frame as a cascade of LZ anti-crossings (solid lines) between nuclear states of alternate electronic manifolds. Dashed lines show corresponding crossings, and dots highlight LZ-LAC points. (b) Equivalent Galton board; isolating LAC points allows us to abstract the system in terms of a Galton board where the crossing points (red) arrange in a 2D checkerboard pattern. Balls striking pegs bounce left or right with probabilities $p$ or $q$, respectively. Driving force is provided by gravity (marked in box). In the analogous Galton board (b), “balls” are nuclear populations, the “pegs” are LACs at which populations bifurcate, and MWs provide the driving force. (c) Transfer matrix description of traversals. It considers a representative section of a larger LAC cascade as in (a), but focused here on only one LAC. Two-component column vectors $p_{k,\ell}$ denote nuclear populations entering (or leaving) the node $(k, \ell)$. Bifurcation (arrows) of the populations is described by the transfer matrix $T_{k,\ell}$ (see Appendix C for details). (e) Analytical evaluation of population evolution. Panels show populations $P_k$ in the 2$^N$ numbered nuclear states in the $m_e = 0$ and $m_e = +1$ manifolds (blue and red points, respectively) upon a full MW sweep following Eq. (7) for $N = 4$ and $N = 8$ (left and right panels) with $p = q = 0.5$ in (b) (see Appendix D 6 for details). Representative nuclear states are marked. Dashed lines represent the hyperpolarization level. (f) Numerical simulation of DOS mapping. Panels show hyperpolarization generated from different sized $\Delta f$ windows, assuming a Gaussian distribution of energy levels in the $m_e = +1$ manifold (see Appendix D 7 for details). Curves track the underlying electronic DOS and become wider with increasing $\Delta f$, as in Fig. 2(b). Forward and reverse sweeps yield positive and negative polarization, respectively (as in Fig. 2(b)).
energy and frequency (axes labeled \( k \) and \( \ell \)) and identify their corresponding energy gaps as \( \varepsilon_{k,\ell} \) (see Appendices B and D, and the supplementary material for details). Upon optical pumping, the initial nuclear populations are equally distributed among nuclear states in the \( m_s = 0 \) manifold. Then, under the MW sweep, the nuclear populations traverse through \( I_{k,\ell} \) and redistribute down or right at every LAC [Fig. 4(b)]. These traversals can be viewed as analogous to the operation of a classical Galton board \cite{57,58} [Fig. 4(c)] in which balls fall through a system of pegs under gravity, encountering which they bounce left or right. In a similar manner, the LACs in Fig. 4(b) form the “pegs,” the “balls” are the nuclear populations, and the swept MWs provide the driving force. The probability of population bifurcation “right” at each LAC is conditioned on the size of the energy gap \( \varepsilon_{k,\ell} \) and given by the tunneling probability \( \eta_{k,\ell} = \exp ( -\varepsilon_{k,\ell} / f_B ) \). Downward bifurcation then has probability \( 1 - \eta_{k,\ell} \). The energy gaps \( \varepsilon_{k,2n-k+1} = \Omega_k \) are the largest on the checkerboard, making traversals through them approximately adiabatic.

We assume that the LACs in Fig. 4(b) are hit sequentially due to the tilted nature of the LAC Galton board and that despite the continuous action of the laser, electronic repolarization happens far away from the LACs. If \( P_{k,\ell}^{k',\ell'} \) and \( P_{k',\ell'}^{k,\ell} \) are two-element column vectors denoting the nuclear populations entering or leaving the \((k,\ell)\) LAC [Fig. 4(d)], then \( P_{k,\ell} = T_{k,\ell} P_{k,\ell}^{k',\ell'} \), where \( T_{k,\ell} = \begin{pmatrix} \eta_{k,\ell} & 1 - \eta_{k,\ell} \\ 1 - \eta_{k,\ell} & \eta_{k,\ell} \end{pmatrix} \) is a transfer matrix \cite{59,60} describing the bifurcation of populations analogous to a Galton board. Traversals through LACs as in Fig. 4(a) can then be recursively solved as \( p_{k,\ell}^{k',\ell'} T_{k,\ell} P_{k,\ell}^{k',\ell'} + T_{k,\ell} M_{k,\ell} P_{k,\ell}^{k',\ell'} \), where the operators \( M_k = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \) and \( M_k = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \) describe “walks” down and right through the \( I_{k,\ell} \) board in Fig. 4(b) (see Appendix C for details). Ultimately, one can quantify the traversal probability between two points with coordinates \((k_i,\ell_i)\) and \((k_f,\ell_f)\) in \( I_{k,\ell} \) as

\[
P( \langle k_i,\ell_i \rangle \rightarrow \langle k_f,\ell_f \rangle ) = \sum_{\{v\} \in L_p} \prod_{j=1}^n C_{v_j},
\]

where \( L_p = \binom{1}{j_{k_f}-k_i} \) represents the total number of paths \( v \) involved, defined by the nearest neighboring vertices such that \( v = \{v_j\} = \{ (k_1,\ell_1), (k_2,\ell_2), \ldots, (k_n,\ell_n) \} \), and the coefficients

\[
C_{v_j} = \begin{cases} 
\eta_{k_j,\ell_j} & \text{if } k_{j-1} = k_{j+1}, \text{ or } \ell_{j-1} = \ell_{j+1}, \\
1 - \eta_{k_j,\ell_j} & \text{if } k_{j-1} \neq k_{j+1} \text{ and } \ell_{j-1} \neq \ell_{j+1}.
\end{cases}
\]

After the action of the laser that resets the NV to \( m_s = 0 \), the population of any nuclear manifold \( S \) is

\[
P_n = p_{2n-2,2n-2}^{2n-2,2n-2}(1) + p_{2n-2,2n-2}^{2n-2,2n-2}(2),
\]

where \( n \in 1 \ldots 2^N \) indices \( S \) in a Hamming ordering. Consequently, the nuclear hyperpolarization \( P \) in Eq. (1) and measured in Fig. 2(a) takes the form

\[
P = \sum_{n=1}^{2^{n-1}} P_n - \sum_{n=2^{n-1}+1}^{2^{n}} P_n
\]

for \( A = 0 \). The alternate case of \( A < 0 \) is shown to produce no hyperpolarization in the \( m_s = +1 \) manifold (see the supplementary material).

Equation (4) can be used to exactly solve for the polarization generated in the simplest case of a single electron coupled to \( ^{13}\text{C} \) (LZ-LAC system in Fig. 5) here for \( A = 0 \) (see Appendices B and D for more details). Upon a MW sweep through the LZ-LAC structure in Fig. 5, a left-to-right traversal occurs. We make the following assumptions that help simplify the theoretical evaluation of traversals, but which are reasonable under the regime of the experiments: (i) the LZ-LACs are assumed to be hit sequentially so that their effects can be evaluated individually, (ii) the nuclear populations are assumed to start in the \( m_s = 0 \) manifold and bifurcate “down” or “right” upon encountering the LZ-LACs, and (iii) NV electronic (re)polarization is assumed to happen far away from the exact LZ-LAC points.

Consider a single traversal from left and right through the \( N = 1 \) LACs in Fig. 5, starting from populations restricted to the \( m_s = 0 \) manifold and ending with NV repolarization. The probabilities of the possible population evolutions are then, as follows:

\[
P( \downarrow \rightarrow \downarrow ) = (1 - \eta_{1,2}) + \eta_{1,2} \eta_{1,1},
\]

\[
P( \downarrow \rightarrow \uparrow ) = \eta_{1,2} (1 - \eta_{1,1}),
\]

\[
P( \uparrow \rightarrow \downarrow ) = \eta_{1,2} (1 - \eta_{1,1}) + 2 \eta_{1,1} (1 - \eta_{1,1}) (1 - \eta_{1,2}),
\]

\[
P( \uparrow \rightarrow \uparrow ) = \eta_{1,1} \eta_{1,2} + 2 \eta_{1,1} (1 - \eta_{1,2}) + (1 - \eta_{1,1})^2 (1 - \eta_{1,2}).
\]

Indeed, each term in the expressions above can be thought of as referring to a different trajectory through the LZ-LAC structure. For instance, there are two paths that constitute the term, \( P( \downarrow \rightarrow \downarrow ) \), corresponding to the probabilities of \( |0,\downarrow \rangle \rightarrow |0,\downarrow \rangle \) and \( |0,\uparrow \rangle \rightarrow |1,\downarrow \rangle \), respectively. Now, in order to determine the nuclear hyperpolarization, we evaluate the difference in populations between the nuclear states at the end of the sweep,

\[
P = [ P( \downarrow \rightarrow \downarrow ) + P( \uparrow \rightarrow \downarrow ) ] - [ P( \downarrow \rightarrow \uparrow ) + P( \uparrow \rightarrow \uparrow ) ] = (1 - \eta_{1,2}) [1 - (2 \eta_{1,1} - 1)^2].
\]
Ultimately, Eq. (5) illustrates that hyperpolarization develops as a result of the differential adiabicity of the traversals through the pairs of LZ-LACs conditioned on the nuclear state. The net hyperpolarization developed in time $T$ has the form

$$P_{\text{net}} = \left[ 1 - \exp\left(-\frac{w_e}{f_r}\right) \right] \cdot T f_r \cdot (1 - \eta_{1,2})\left[1 - (2\eta_{1,1} - 1)^2\right],$$

(6)

where the first term encapsulates the starting electron polarization (here, $w_e$ is the rate of electron polarization), the second term gives the total sweeps in time $T$, and the last term is Eq. (5). We, therefore, refer to the mechanism as being a "spin-ratchet" since each MW sweep event can be thought of as performing work to transfer a finite amount of polarization from the electronic spin to the directly coupled nuclei. While Eq. (6) is derived from the $N = 1$ case displayed in Fig. 5, it acts as a good approximation even at large $N$ (Ref. 63).

Surprisingly, this same procedure can also be used to tractably solve for polarization generated in the coupled $e$-($n$)$^N$ system in Fig. 1(a), which is a key result of this work. It permits for an analytical (or numerical) means to evaluate traversals through the full $I_{k,\ell}$, $e$-($n$)$^N$ system displayed in Fig. 5, or in narrow $\Delta f$ window through it [as in Fig. 2(a)]. Consider first the solution of the full sweep through $I_{k,\ell}$. Assuming the probability of redistribution down and right to be $p$ and $q$, respectively, at every LAC and that the large energy gaps yield adiabatic traversals ($\eta_k = 0$), assumptions that do not alter the essential physics of the problem, the probability of ending in the nuclear state $n \in S$ after a full MW sweep can be analytically written as (see the supplementary material for details)

$$P_n = \frac{1}{2^N} \sum_{\ell=1}^{2^{N-1}} \left[ \binom{n + 2 - \ell}{2^{N-\ell} - q} \left( \binom{n - 2}{2^{N-\ell} - p} + \binom{2^{N-\ell} - q}{2^{N-\ell} - p} \left( \binom{n - 2}{2^{N-\ell} - p} + \binom{n - 2}{2^{N-\ell} - p} \right) \right) \right] + c(n),$$

(7)

where $\binom{a}{b}$ represents the combinatoric operator and $c(n)$ is a constant equal to 1 when $n = 1$ and 0 otherwise (see Appendix D for more details). Equation (7) alludes to the binomial nature of Galton board traversals and provides insights into the physics of the polarization transfer process. Solutions to $N = 4$ and $N = 8$ are displayed in Fig. 4(e), showing populations of the numbered nuclear states in the $m_0 = 0$ and $m_1 = 1$ manifolds (blue and red points, respectively). Representative nuclear states are marked. As is evident, traversal through the Galton board in Fig. 4(b) is "biased," resulting in the hyperpolarization $P$ denoted by the horizontal dashed lines in Fig. 4(e).

In a similar manner, one can carry out calculations of traversal through a narrow $\Delta f$ window on the LZ Galton board. While an analytic solution is tractable, it is unwieldy, and here, we resort to a numerical solution assuming an exemplary Gaussian distribution of energy levels $g$ (with width 13.5 MHz) in the $m_0 = 1$ manifold as in Fig. 1(b) (see Appendix D for more details). The edge of the window ($f_e$) is swept in an analogous fashion to the experiments in Fig. 2(a), and nuclear populations are calculated following Eqs. (2)–(4). Figure 4(f) demonstrates the result for varying $\Delta f$ and under alternate sweep conditions. We observe that the polarization levels $P$ approximately track the Gaussian DOS $\delta g$, qualitatively matching the experimental results in Fig. 2. Intuitively, this is because the Galton board operation "moves" nuclear populations following the underlying distribution $\delta g$. Larger $\Delta f$ windows [panels left-to-right in Fig. 4(f)] yield a broader spectrum, and opposite sweeps produce an alternate hyperpolarization sign [Fig. 4(i)]. These match the experimental observations in Figs. 2(b) and 2(h).

VI. THEORETICAL OUTLOOK

The formalism developed here allows one to model the effect of a driven N-spin quantum system undergoing evolution through a cascaded series of level anti-crossings. Given that the number of anti-crossings scales exponentially with system size $\propto 2^{N^2}$, this problem appears intractable at first. However, the description in terms of traversals of an analogous “Galton board” permits both analytic and numeric solutions, allowing one to extract physically relevant information in the large $N$ limit. The cascaded LZ-LAC structure studied here (Fig. 4) is a motif that occurs commonly in several contexts, such as in quantum walks in Hilbert spaces and operator scrambling, as well as in applications such as BosonSampling that involve multiple cascaded Mach–Zehnder interferometer traversals (see Appendix D). We, therefore, envision that the approach developed here might contribute means to employ engineered central spin systems to study these phenomena.

More direct applications of this theoretical framework lie in the mechanistic description of dynamic nuclear polarization (DNP) in the large nuclear spin limit, the predominant experimental regime of interest. Our work shows a systematic approach to extend DNP models beyond standard descriptions of $e$-$n$ or $e$-$e$-$n$ systems and can inform physics at large $N$.

VII. CONCLUSION

In this work, we demonstrated a technique to read out electronic spectra by mapping them to spin population differences in surrounding nuclear spins via DNP. Interestingly, this indirect spectral map displayed signatures of first-shell $^{13}C$ nuclei, which are otherwise undetectable. Furthermore, our results indicate that the rates of polarization transfer from these first-shell nuclei are not significantly different from the rate of direct polarization of the bulk nuclei, an unexpected result indicating the absence of a spin diffusion barrier. This supports recent data from experiments in Refs. 81–83, which pointed to the absence of a spin diffusion barrier in similar scenarios.

We applied the developed spectral map to imprint the NV center spectrum $g$ into the $^{13}C$ spin polarization levels. We then demonstrated a practical application in underwater bulk-diamond...
DC magnetometry. We envision applications of the spectral mapping technique introduced here to a broader class of hybrid quantum systems.

We also theoretically addressed the mechanism of optical DNP in a central spin system. We described how the system can be described by traversals through a cascade of Landau–Zener anti-crossings, giving insights into the development of “bias” in the traversals that then leads to hyperpolarization. Ultimately, we demonstrate how the polarization developed during DNP ends up tracking the electronic spectra Fig. 2(a), allowing the nuclear spins to indirectly report on the underlying electronic spectrum. Overall, the DNP mechanism here can be understood as a variation of the mechanism at play in the Integrated Solid Effect.24

We envision that our work can be easily extended to problems involving traversals through a series of cascaded energy crossings in other systems, with applications in DNP,25 spin qubit, or resonator “cooling”26,27 and in quantum sensing and information processing with central-spin systems.

SUPPLEMENTARY MATERIAL

See the supplementary material for calculations of the energy gaps and their native hierarchy and additional data.

ACKNOWLEDGMENTS

We acknowledge discussions with J. Reimer, S. Bhave, P. Zangara, C. Meriles, and D. Suter. A. A. acknowledges funding from ONR (N00014-20-1-2806), AFOSR (22RT0619) and CIFAR Azrieli Global Scholars Fellowship (GS23-013).

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Arjun Pillai: Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). Monish Elanchezian: Data curation (equal); Formal analysis (equal); Methodology (equal); Software (equal); Validation (equal); Visualization (equal). Teemu Virtanen: Formal analysis (equal); Software (equal). Sophie Conti: Visualization (equal). Ashok Ajoy: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Resources (equal); Software (equal); Supervision (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

APPENDIX A: SUMMARY OF THEORETICAL APPROACH

In Appendices A–D, we present a more detailed version of the theory summarized in the main paper. Figures 4(a), 4(b), and 6 summarize the basic theoretical approach. The problem of solving the hyperpolarization dynamics becomes that of tracking the populations in a system as they encounter a cascade of LZ-LACs under a MW sweep. The exponentially scaling number of anti-crossings ($\approx 2^{2N}$) makes this problem challenging; however, with some approximations (detailed below), the dynamics can be restricted to that of populations at the LZ points alone [Fig. 4(b)].

Our solution entails building an analogy to the operation of a Galton board. Consider the LZ checkerboard in Fig. 6. At $t = 0$, the nuclear populations are equally distributed along the levels of the $m_z = 0$ manifold. Upon encountering an LZ point, however, they are redistributed with a finite probability either “right” or “down” on the checkerboard $I_{kL}$ with the probability defined by the size of the local LZ energy gap. Tracking the population dynamics can now be handled with a transfer matrix formalism for any specific trajectory traversed through the LZ checkerboard. If $v$ defines a path through $n$ points in the 2D checkerboard (black arrow in Fig. 6) with coordinates $v = \{v_j\} = \{(k_1, \ell_1), (k_2, \ell_2), \ldots, (k_n, \ell_n)\}$ [see Fig. 6(b)] and

![FIG. 6. Galton board of Landau–Zener LACs. (a) The Landau–Zener LACs for a representative case of an NV center coupled to $N = 4$ $^{13}$C nuclei and positive $A_0^\parallel$. Representative nuclear states are marked. The LZ-LACs (dots) form the $I_{kL}$ checkerboard as in Fig. 4(b), where coordinates mark their individual positions. Axes $(k, \ell)$ refer to energy and frequency, respectively. The center of the checkerboard is marked $O$, and the conjugate diagonal (dashed line) refers to positions $I_{kL}^{k^\perp, \ell^\perp}$. Eigenstates corresponding to the diagonal Hamiltonian $\hat{H}_{\text{diag}}$ are labeled (see Fig. 7). At $t = 0$, populations start equally distributed among the nuclear states restricted to the $m_z = 0$ manifold. A MW sweep causes the system to encounter the LZ-LACs in a sequential manner. The black arrow shows an exemplary trajectory $v$ through the checkerboard. (b) Zoom-in to a section (blue dashed box) of the checkerboard showing specific vertices $v_j$ forming the trajectory $v$. Nuclear populations are redistributed at every LZ-LAC similar to the operation of a Galton board [Fig. 4(c)].]
\( \mathbf{p}_m (\mathbf{p}_f) \) are column vectors denoting nuclear populations at the initial (final) LZ point, traversals can be evaluated analogous to the operation of a Galton machine,

\[
\mathbf{p}_f = T_v M_{(v_1, v_2, \ldots)} \cdots T_v M_{(v_f, v_{f-1})} T_v M_{(v_1, v_2)} T_v \mathbf{p}_i,
\]

where \( T_v \) is a "redistribution" operator at the LZ point \( v_f \) and \( M_{(v_i, v_{i-1})} \) and \( M \) are "walk" operators connecting the nearest neighbor points that define the path \( v \). Through this simple map, we demonstrate the origin of bias in the traversals, which is responsible for nuclear hyperpolarization. We then show that DNP carried out in small windows \( B \) of the electronic spectrum occurs such that the hyperpolarization follows the electronic DOS, a reflection of the experimental data in Fig. 2(a).

**APPENDIX B: SYSTEM OF CASCADED LANDAU-ZENER LACs**

1. Central spin system and hyperpolarization protocol

The NV-\(^{13}\)C system is considered here as a model of a hybrid e-n system that captures two commonly encountered features reflected in Fig. 1(a).

(i) The electron concentration is orders of magnitude more dilute than that of the nuclear spins, and thus, inter-electron couplings can be neglected.

(ii) Nuclear \( T_m \) is far exceeds that of the electron and polarization can be made to accumulate in the nuclear through repeated polarization transfer from the electron.

In our samples [e.g., as employed in Fig. 2(a)], the NV centers are surrounded by an average of \( \approx 10^4 \) \(^{13}\)C nuclei, and inter-electron spacings are \( r_C \approx 12 \) nm. If \( w_L \) defines the rate of NV electronic polarization buildup, the electron polarization follows as \( P_e (\tau) = 1 - \exp\left(-w_L \tau\right) \). At sufficiently high optical powers, \( w_L \) is set by the intensity of the laser illumination applied. At low powers, however, \( w_L \approx T_C^{-1} \), the electron polarization rate is then set by just the thermal reorientation rate.

2. NV-\(^{13}\)C system Hamiltonian

The cascade of LZ-LACs as in Figs. 4(a) and 6 originates from diagonalizing the instantaneous system Hamiltonian,

\[
\mathcal{H}_{\text{tot}}(t) = \mathcal{H} + \mathcal{H}_{\text{MW}}(t),
\]

at every step of the applied frequency sweep. The two terms here refer to the spin Hamiltonian and applied chirped MW control, respectively. The latter has the form

\[
\mathcal{H}_{\text{MW}}(t) = \Omega z \mathbf{S}_e \cos (\omega_{\text{MW}} t),
\]

where \( \mathbf{S}_e \) is a spin-1 Pauli operator and \( \Omega z \) is the electronic Rabi frequency. The instantaneous MW frequency, \( \omega_{\text{MW}}(t) \), is of the form

\[
\omega_{\text{MW}}(t) = 2\pi (B_j t + f_0 - B/2),
\]

where \( f_0 \) is the sweep repetition rate [Fig. 1(c)]. We will focus here on a scenario as in Fig. 1(a), considering a system of \( N \) \(^{13}\)C nuclear spins directly hyperfine-coupled to an NV center with hyperfine strength \( [A_j] \), where \( j = 1, \ldots, N \). We ignore dipolar couplings between the \(^{13}\)C nuclei, focusing, instead, on a direct NV \( \rightarrow \) \(^{13}\)C polarization transfer process. In the low-field DNP regime, the bare \(^{13}\)C Larmor frequency is smaller than or comparable to the strength of the hyperfine couplings, \( \omega_L = \gamma_B B_0 \lesssim [A_j]^{1/2} \), where \( \gamma_B = 1.07 \) kHz/G is the nuclear magnetogyric ratio.

Now, considering the spin Hamiltonian \( \mathcal{H} \) for a system of \( N^{13}\)C nuclear spins hyperfine-coupled to the NV center as in Fig. 1(a), it is convenient to consider the nuclear Hamiltonian selectively in each NV manifold. We focus here just on the two-level system formed by the \( m_s = \{0, +1\} \) manifolds [see Fig. 1(b)]. We assume for simplicity that \( B_0 \) is aligned with the NV axis, a direction we label \( z \). We separate the hyperfine field into its longitudinal and transverse components, \( A_j = A_j^l z + A_j^o \perp z \), where \( \perp \) is a unit-vector in the xy plane. Some comments are worth noting.

(i) Experiments [e.g., Fig. 2(a)] are performed in the ensemble limit, and thus, to a good approximation, there is an equal probability of spins with positive or negative \( A_j^l \) couplings.

(ii) The \( m_s = 0 \) NV state is "non-magnetic," and the nuclear spins are predominantly quantized here in the Zeeman field \( B_0 \). In reality, there is a weak additional second-order coupling mediated by the hyperfine term, leading to an effective nuclear frequency in the \( m_s = 0 \) manifold, \( \omega_f^{(0)} = \omega_L + \gamma_B B_0 \), where \( \Delta = 2.87 \) GHz is the NV center zero field splitting. The nuclear Hamiltonian in the \( m_s = 0 \) manifold is then of the form \( \mathcal{H}_n = \sum_{j=1}^N \omega_f^{(0)} I_j \), where \( I \) are spin-1/2 Pauli operators.

(iii) In the \( m_s = +1 \) manifold, on the other hand, there is a combined action of the Zeeman and hyperfine fields, \( \omega_f^{(1)} = \sqrt{(\omega_L + A_j^l)^2 + (A_j^o)^2} \). Indeed, the quantization axis \( z' \) here need not be collinear with \( B_0 \); in general, \( z' = \hat{z} \cos \phi_j + \hat{x} \sin \phi_j \), where the angle \( \phi_j = \tan^{-1}\left[ A_j^l / (\omega_L + A_j^o)\right] \). The \( m_s = +1 \) nuclear Hamiltonian is then of the form \( \mathcal{H}_n = \sum_{j=1}^N \omega_f^{(1)} I'_j \), where \( I'_j = I_j \cos \phi_j + I_0 \sin \phi_j \).

Going into a rotating frame with respect to \( \hat{z} \) at frequency \( \omega_{\text{MW}} \) gives the net system Hamiltonian in Eq. (B1),

\[
\mathcal{H}_{\text{tot}}(\omega_{\text{MW}}) = (\Delta - 2\omega_{\text{MW}}) \mathbf{S}_z + \gamma_B B_0 \mathbf{S}_z + \Omega z \mathbf{S}_e \cos (\omega_{\text{MW}} t)
\]

\[
+ \sum_{j=1}^N \left[ \omega_f^{(0)} P_0 I_j + \omega_f^{(1)} P_1 I'_j \right],
\]

where \( P_0 = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \otimes \mathbf{1}_N, P_1 = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \otimes \mathbf{1}_N \) are the respective projection operators to the NV manifolds and \( \mathbf{1}_N \) is a unit operator on the nuclear spins.

3. Eigenstates and eigenenergies

Plotted with respect to the instantaneous frequency \( \omega_{\text{MW}} \), the eigenvalues of \( \mathcal{H}_{\text{tot}} \) in Eq. (B4) undergo a sequence of cascaded LZ-LACs [as in Figs. 4(a) and 6]. To determine their positions, our strategy will be to first calculate the crossing points, focusing only on the diagonal Hamiltonian, and subsequently promoting them to
anti-crossings by including off-diagonal terms (see Fig. 7). To this end, consider first separating $H_{\text{tot}}$ into its diagonal and off-diagonal parts, $H_{\text{diag}}(\omega_{\text{MW}}) = H_{\text{diag}}(\omega_{\text{MW}}) + H_{\text{non-diag}}$, where

$$H_{\text{diag}}(\omega_{\text{MW}}) = (\Delta - \omega_{\text{MW}}) S_z^0 + \gamma_e B_0 S_z + \sum_{j=1}^{N} \left[ \omega_j^{(0)} p_j^0 I_{zj} + \omega_j^{(1)} p_j^1 I_{zj} \cos \phi_j \right], \quad (B5)$$

$$H_{\text{non-diag}} = \Omega_c S_x + \sum_{j=1}^{N} \omega_j^{(1)} p_j^1 I_{zj} \sin \phi_j. \quad (B6)$$

The latter encapsulates contributions from $\{\Omega_c, A_j^+\}$ terms. Considering only $H_{\text{diag}}$ allows us to label the eigenstates [Fig. 4(b)] and identify points at which LZ-LACs will ultimately arise (see also Figs. 6 and 7). Specifically, in Figs. 7(a)–7(d), we show the systematic emergence of the LZ-LACs in a series of steps highlighted in the insets.

(i) Considering $H_{\text{diag}}$, but with only the Zeeman terms of the electron and nuclear spins [Fig. 7(a)].

(ii) Considering $H_{\text{diag}}$ but including the hyperfine terms [Fig. 7(b)] results in the crossing points that closely define the checkerboard $Z_{N,F}$ as in Fig. 4(b).

(iii) Including the Rabi term from $H_{\text{non-diag}}$ [see Fig. 7(c)] results in a set of anti-crossings at many former crossing points, here corresponding to levels where the electronic, but not the nuclear, states change.

(iv) Finally, including the full extent of off-diagonal terms in $H_{\text{non-diag}}$ [Fig. 7(d)] gives rise to anti-crossings at each of the former crossing points, although with differing energy gaps (described in Appendix B 5 and the supplementary material).

To label eigenstates in Eq. (B5), we assume that $S$ labels the $2^N$ possible nuclear spin states in each electronic manifold consisting of all combinations of spin up or down. For instance, for $N = 2$, we have $S = \{|\downarrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\uparrow\uparrow\rangle\}$. These also correspond to the eigenstates of the diagonal Hamiltonian $H_{\text{diag}}$. Using the Hamming binary notation with $h_i = 0$ or 1 representing $|\uparrow\rangle$ or $|\downarrow\rangle$, respectively, the eigenenergies of the diagonal Hamiltonian in the $m_z = \{0, +1\}$ manifolds take the forms

$$E_j^{(0)}(\omega_{\text{MW}}) = \sum_{j=1}^{N} (-1)^{h_j} \omega_j^{(0)}, \quad (B7)$$

$$E_j^{(1)}(\omega_{\text{MW}}) = (\Delta + \gamma_e B_0 - \omega_{\text{MW}}) + \sum_{j=1}^{N} (-1)^{h_j} \omega_j^{(1)}. \quad (B8)$$

This allows us to constrain the locations of the LZ-LACs in the checkerboard. The index $J$ here runs over $2^N$, and we note from Eq. (B7) that the eigenvalues are independent of $\omega_{\text{MW}}$ in the $m_z = 0$ manifold and scale linearly with it in the $m_z = +1$ case [Eq. (B8)].

While the discussion here is applicable for an arbitrary hyperfine network $A_j^+-A_j^-$, in this paper, we consider an exemplary scenario where hyperfine couplings are in a non-degenerate configuration such that

$$\omega_j^{(0)} = j^p, \quad \omega_j^{(1)} = \alpha j^p. \quad (B9)$$

For example, in Fig. 7, we employ this model with $\alpha = 5$ and the exponent $p = 1.1$. The lack of degeneracies in this model illuminates

**FIG. 7.** Emergence of cascaded Landau–Zener LACs described in a systematic manner for an NV center coupled to $N = 3$ $^{13}$C nuclei in a magnetic field $B_0$ [see Fig. 1(a)] using the model in Eq. (B9). We focus on the $m_z = \{0, +1\}$ electronic manifolds and introduce Hamiltonian terms hierarchically to illustrate the physical origin of the LZ-LACs (shaded insets). (a) Considering only the diagonal Hamiltonian $H_{\text{diag}}$ [Eq. (B5)] with $A_j^+ = 0$ and (b) with finite $A_j^+$. There are $2^N$ crossing points between nuclear states in the two electronic manifolds, labeled here by the corresponding eigenstates (shown are representative states). (c) Including now the Rabi frequency term $\Omega_c$ from $H_{\text{non-diag}}$ [Eq. (B6)] leads to LZ-LACs between states on the conjugate diagonal (see Fig. 6) involving a direct electronic spin flip $|0, S\rangle \leftrightarrow |+1, S\rangle$ for any nuclear state $S$. (d) Finally, considering the full Hamiltonian $H_{\text{tot}}$ [Eq. (B4)], LZ-LACs appear at each crossing point. The corresponding energy gaps display the native hierarchy based on the total number of spin flips they involve.

J. Chem. Phys. 159, 154201 (2023); doi: 10.1063/5.0157954
the physics of LZ traversals more clearly, while the same general principles follow in the degenerate case as well.

4. Checkerboard of anti-crossings \( I_{k,\ell} \)

Let us now return to the situation in Fig. 7(b) and determine the exact positions of the LZ-LACs. Eigenergies in each of the \( m_i = \{0, +1\} \) manifolds form separate sets of parallel lines, and lines corresponding to different manifolds intersect. For \( N \) nuclear spins connected to the central NV center, there are, in general, \( 2^{2N} \) crossing points. Together, these crossing points form the checkerboard pattern \( I_{k,\ell} \) [as in Figs. 4(b) and 6] in the 2D plot of energy and frequency.

Let \( I \) refer to the matrix of coordinates of these crossing points in a diagram as in Fig. 6, where the abscissa \( I_{k,\ell}(1) \) and ordinate \( I_{k,\ell}(2) \) refer to frequency and energy, respectively. The label indices \( k, \ell \in 1 \ldots 2^N \) refer to levels in the \( m_i = +1 \) and \( m_i = 0 \) manifolds, respectively. We arrange the crossings from left-to-right and top-to-bottom (i.e., increasing in frequency and descending in energy). Referring to Fig. 6, the element \( I_{1,1} \), for instance, refers to the crossing between levels \( |0, ↑↑↑↑\rangle \) and \( |+1, ↓↓↓↓\rangle \). Following this convention, the elements can be written as

\[
I_{k,\ell} = \left( E_k^{(1)}(0) - E_\ell^{(0)} - E_\ell^{(0)} \right),
\]

(B10)

given that from Eq. (B7),

\[
E_k^{(1)}(\omega_{MW}) = E_k^{(1)}(0) - \omega_{MW},
\]

(B11)

and thus, at the LZ-LACs,

\[
\omega_{MW} = E_k^{(1)}(0) - E_\ell^{(0)}.
\]

(B12)

For instance, the LZ-LAC \( I_{2,1} \) is formed from the intersection of two levels in the \( m_i = \{0, +1\} \) manifolds. The \( I_{k,\ell} \) checkerboard pattern is displayed in Figs. 4(b) and 6, and is tilted since the crossings corresponding to lower nuclear states occur at higher frequency, \( I_{2,1}(1) > I_{2,1}(1) \). A key consequence is that the system, upon a MW sweep, encounters LZ-LACs in a sequential manner [Fig. 4(b)]—important for ultimately causing “bits” in the nuclear polarization buildup.

5. LACs: Energy gaps, symmetries, and hierarchies

Continuing our discussion onto Figs. 7(c) and 7(d), we now elucidate the emergence of the LZ-LACs and their associated energy gaps. We will refer to the checkerboard energy gaps at positions \( (k, \ell) \) as \( \varepsilon_{k,\ell} \) using the same notation convention as above. The gaps arise approximately at the abcissa locations marked by \( I_{k,\ell}(1) \). Numerically extracted gap center locations are plotted as points in Figs. 4(b) and 6, while the dashed lines refer to the checkerboard crossing points obtained using an approach similar to Fig. 7(c). For simplicity, we refer to the \( I_{k,\ell} \) positions on the checkerboard as those on the diagonal, while those at the positions \( I_{k,\ell} \) belong to the “conjugate diagonal” (see Fig. 6).

To intuitively unravel the formation of the LZ-LACs, consider first the action of the Rabi frequency term \( \Omega_k \), as in Fig. 7(c). Energy gaps open up only at the conjugate diagonal (for positive \( A \)), corresponding to the anti-crossings between states \( |0, S\rangle \rightarrow |+1, S\rangle \), where \( S \) is any state of the nuclear spins. The energy gaps here \( \varepsilon_{k,\ell} = \Omega_k \) since this transition just corresponds to a single electron flip—akin to the situation encountered in a rapid adiabatic passage over the electrons. Including the perpendicular hyperfine terms \( A_j \) in Eq. (B6) provides additional LZ-LACs at each of the \( I_{k,\ell} \) crossing points in Fig. 7(d).

Section I of the supplementary material shows a detailed evaluation of the corresponding gaps, but we comment here that they satisfy two mirror symmetry conditions (evident in Fig. 6),

\[
|O - I_{k,\ell}| = |O - I_{k',\ell', -k, -\ell + 1}| , \hspace{1cm} (B13)
\]

\[
\varepsilon_{k,\ell} = \varepsilon_{k',\ell', -k, -\ell + 1}, \hspace{1cm} (B14)
\]

(i) The first condition [Eq. (B13)] describes a mirror symmetry of the checkerboard diagram with respect to the center \( O = (A + y_\ell B, 0) \) (see Fig. 6), a consequence of the spin-1/2 \( ^{13}\text{C} \) nuclei and the fact that all \( A \) are positive in the chosen model in Eq. (B9).

(ii) Similarly, Eq. (B14) elucidates a symmetry in the energy gaps about the conjugate diagonal on the checkerboard (see Fig. 6). For instance, the gaps corresponding to LZ-LACs \( |0, ↑↑↑↑\rangle \leftrightarrow |+1, ↓↓↓↓\rangle \) and \( |0, ↓↓↓↓\rangle \leftrightarrow |+1, ↑↑↑↑\rangle \) should be identical because they just differ in an exchange between nuclear labels undergoing the crossing.

\section*{APPENDIX C: TRANSFER MATRIX FORMALISM}

\subsection*{1. Traversals through cascaded Landau-Zener LACs}

We now develop the analogy with the Galton board [see Figs. 4(b) and 4(c)] to evaluate the evolution of nuclear populations through the checkerboard \( I_{k,\ell} \) and show how this evolution yields nuclear hyperpolarization. We make two operational assumptions.

(i) The \( I_{k,\ell} \) LZ-LAC points are assumed to be hit sequentially, and their effects are evaluated individually. This is reasonable if the energy gaps \( \varepsilon_{k,\ell} \) are small compared to their frequency separation.

(ii) NV (re)polarization is assumed to happen far away from the exact LZ-LAC points \( I_{k,\ell} \), a good approximation when \( \varepsilon_{k,\ell} < B \). This allows us to consider the LZ system traversals independent of optical pumping.

At each checkerboard point, let \( p_{k,\ell}^{-} \) and \( p_{k,\ell}^{+} \) denote the nuclear populations of the two states undergoing the LZ-LAC, before and after the anti-crossing is encountered. This is shown in Fig. 8 for four LZ crossings in a \( 2 \times 2 \) portion of the \( I_{k,\ell} \) checkerboard. We denote the populations as column vectors, with the first (second) element referring to nuclear populations in the \( m_i = 0 \) (\(+1\)) manifolds, respectively,

\[
p_{\ell,\ell}^{-} = \begin{bmatrix} p_{k,\ell}^{-}(1) \\ p_{k,\ell}^{-}(2) \end{bmatrix}, \hspace{1cm} p_{\ell,\ell}^{+} = \begin{bmatrix} p_{k,\ell}^{+}(1) \\ p_{k,\ell}^{+}(2) \end{bmatrix}.
\]

(C1)

The effect of any chosen trajectory through (as in Fig. 6) the LZ cascade can then be built out of simple \( 2 \times 2 \) matrices. Evolution starts...
with the population restricted to the $m_s = 0$ manifold and with the $\frac{1}{2}$C nuclear spins in a mixed state $1_N$. This means that each of the nuclear states in the $m_s = 0$ manifold has an equal initial starting probability. Traversal can be then be calculated by considering populations starting with the initial states $p_{k,\ell} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and averaging the result over the $3N - 1$ states.

2. Transfer matrix formalism

Consider first the action of a single LZ-LAC point $T_{k,\ell}$ with energy gap $\Delta_{k,\ell}$. Encountering it leads to a rearrangement of nuclear populations,

$$
\begin{align*}
\eta_{k,\ell}^+ (1) &= \eta_{k,\ell} \eta_{k,\ell} (1) + (1 - \eta_{k,\ell}) \eta_{k,\ell} (2), \\
\eta_{k,\ell}^- (2) &= (1 - \eta_{k,\ell}) \eta_{k,\ell} (1) + \eta_{k,\ell} \eta_{k,\ell} (2),
\end{align*}
$$

where $\eta_{k,\ell}$ refers to the tunneling probability through the anti-crossing and has the form

$$
\eta_{k,\ell} = \exp \left( -\frac{\epsilon_{k,\ell}}{f_s} \right).$

Equation (C2) can then be recast in terms of a transfer matrix $T_{k,\ell}$,

$$
p_{k,\ell} = T_{k,\ell} p_{k,\ell},
$$

where

$$
T_{k,\ell} = \begin{pmatrix} \eta_{k,\ell}^- (1) & 1 - \eta_{k,\ell}^- (1) \\ 1 - \eta_{k,\ell}^- (2) & \eta_{k,\ell}^- (2) \end{pmatrix}.$$

$T_{k,\ell}$ plays the role of a “redistribution” operator since it causes the rearrangement of populations at the $T_{k,\ell}$ anti-crossing points (Fig. 8). Traversal is adiabatic if $f_s B_{\ell,\ell}^s \ll 1$ and diabatic if $f_s B_{\ell,\ell}^s \gg 1$. In the limiting case when the gap is large ($\eta_{k,\ell} \to 0$) and there is a complete transfer of population between the states at the LZ-LAC, $T_{k,\ell} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$. On the other hand, for a purely diabatic transfer, $T_{k,\ell} = I_2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$, and the populations are preserved. In a more generic, yet diabatic case, there is a bifurcation of populations at the $T_{k,\ell}$ crossing point (Fig. 8). Note that the matrix formulation above only considers the redistribution of nuclear populations at each LZ-LAC and ignores coherences. In reality, there is a phase picked up by the quantum state as it traverses through an LZ-LAC. However, in our experiments (to a good approximation), this phase can be ignored because the following holds:

(i) In the high defect density sample we consider in Fig. 2, the electronic $T_{2e} \sim 50$ ns $\ll f_s^{-1}$ and much smaller than the single sweep time $f_s^{-1}$ as well as the traversal time between successive $T_{k,\ell}$ points.

(ii) The bare nuclear coherence time over which electrons are repolarized—$T_{2n} \sim 1$ ms—is of the order of the sweep period, but much smaller than the total polarization time (which involves $>10^3$ sweeps) [Fig. 1(c)]. To a good approximation, then, any nuclear coherence produced as a result of the traversal rapidly dies away due to internuclear interactions.

(iii) In experiments [Fig. 2(a)], we perform an ensemble average over a large collection of $e-n$ systems, such as in Fig. 1(a). In this case, the coherence of the electronic state can be considered randomized and one can consider only the redistributions of state populations at each LZ-LAC.

Equations (C4) and (C5) make more concrete the analogy to the Galton board [Figs. 4(b) and 4(c)]. A classical Galton board operates through balls falling through a system of pegs under gravity [see Fig. 4(c)]. At each peg, the balls can bounce left or right (usually with 50% probability each). In a similar manner, the LZ-LACs here form the “pegs,” the “balls” are the nuclear populations, and the swept MWs provide the driving force analogous to gravity [Fig. 4(b)]. The LZ Galton board here is tilted, and the nuclear populations bounce at each LZ-LAC either right or down, the probability being conditioned on the size of the corresponding energy gap $\epsilon_{k,\ell}$.

Building on this analogy, let us now evaluate the action of sequentially encountering LZ anti-crossings under a low-to-high frequency MW sweep. Extending Eq. (C4), the net traversal can then
be written as a product of transfer matrices corresponding to a trajectory through the cascaded LZ-LACs. Since there is no population evolution between successive LZ-LACs, \( p_{k,0}^+ = p_{k-1,0}^+ \) and \( p_{k,1}^- = p_{k-1,1}^- \). Therefore, Eq. (C4) can be rewritten as

\[
\begin{align*}
p_{k,1}^+ &= T_{k,1} M_k p_{k-2,1}^+ + T_{k,2} M_k p_{k-1,1}^+ + T_{k,3} M_k p_{k-2,1}^- + T_{k,4} M_k p_{k-1,1}^- \\
p_{k,0}^- &= T_{k,0} M_k p_{k-2,1}^- + T_{k,2} M_k p_{k-1,1}^- 
\end{align*}
\]  
(C6)

or equivalently,

\[
\begin{align*}
p_{k,1}^+ &= T_{k,1} M_k p_{k-2,1}^+ + T_{k,2} M_k p_{k-1,1}^+ \\
p_{k,0}^- &= T_{k,0} M_k p_{k-2,1}^- + T_{k,2} M_k p_{k-1,1}^- 
\end{align*}
\]  
(C7)

where we define the "walk" operators,

\[
M_L = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}, \quad M_R = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}
\]  
(C8)

\( M_L \) and \( M_R \) refer to walks over the checkerboard by a single-step "down" or "right," respectively. Equation (C7) is interesting because it connects populations at \( L \)-LAC sites \((k, \ell)\) with prior nearest neighbor sites on the checkerboard, schematically described in Fig. 8. Combining Eqs. (C4) and (C7) provides the recursive relationship

\[
p_{k,1}^+ = T_{k,1} M_k p_{k-1,1}^+ + T_{k,2} M_k p_{k-1,0}^+ \\
p_{k,0}^- = T_{k,0} M_k p_{k-1,0}^-
\]  
(C9)

which connects an \( I_{k,1} \) checkerboard point to its nearest and next-nearest neighbors (see Fig. 8). This process can be continued to encompass every path of evolution through the cascaded LZ system. Consider, for instance, the portion of the trajectory \( v \) (black line) in Fig. 6(b). The final nuclear population through it is, then,

\[
p_{v,1} = T_{v,1} p_{1,1}^-, \quad \text{where} \quad p_{1,1}^- = \begin{pmatrix} 1 \\ 0 \end{pmatrix}
\]  
(C10)

In general, consider a path consisting of a sequence of nearest neighbor points through \( I_{k,1} \): \( v = \{v_j\} = \{(k_1, \ell_1), \ldots, (k_n, \ell_n)\} \). If \( p_i^- \) and \( p_j^+ \) are the populations at the initial and final coordinates, respectively, this recursive condition can be generalized,

\[
p_j^+ = T_{v_j} M_{(v_{j+1},v_j)} T_{v_{j+1}} M_{(v_{j+2},v_{j+1})} \cdots T_{v_2} M_{(v_{3},v_2)} T_{v_1} M_{(v_2,v_1)} p_{v_1}^-
\]  
(C11)

where \( T_{v_j} \) is the corresponding bounce operator at coordinate \( v_j = (k_j, \ell_j) \), and the operator \( M \) refers to the walk through the checkerboard,

\[
M_{(v_{j+1},v_j)} = \begin{cases} 
M_L & \text{for } k_{j+1} = k_j + 1, \\
M_R & \text{for } \ell_{j+1} = \ell_j + 1,
\end{cases}
\]  
(C12)

based on whether the subsequent trajectory entails a movement right or down in the board. From Eqs. (C7) and (C8) and since \( p_i = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \), it is now possible to evaluate the final probability of the path defined by the coordinates \( v = \{v_j\} \) as

\[
P = \prod_{j=1}^n C_{v_j},
\]  
(C13)

with coefficients

\[
C_{v_j} = \begin{cases} 
\eta_{k_j,\ell_j} & \text{if } k_{j-1} = k_j + 1 \text{ or } \ell_{j-1} = \ell_j + 1, \\
\left(1 - \eta_{k_j,\ell_j}\right) & \text{if } k_{j-1} \neq k_j + 1 \text{ and } \ell_{j-1} \neq \ell_j + 1.
\end{cases}
\]  
(C14)

These two factors entering Eq. (C13) can be intuitively understood. If at a specific \( L \)-LAC the trajectory \( v \) involves a path that continues straight and does not take a "bend," then the term that enters the product is the direct tunneling probability \( \eta_{k,\ell} \). Alternatively, a bend appears with the factor \((1 - \eta_{k,\ell})\). This allows for the final probability \( P \) (and thus final population) for any path to be easily found. For simplicity, we decompose \( P \) at any \( L \)-LAC point into two components, \( P = [P^{(1)}, P^{(2)}]^T \), with \( P^{(1)} \) representing final \( m_i = 0 \) populations and \( P^{(2)} \) representing final \( m_i = 1 \) populations (see Fig. 9). For instance, when applied to the full trajectory \( v \) in

\[\text{FIG. 9. Calculation schematic for transfer probability } P. \text{ Representative } LZ \text{ Galton board showing a schematic of population evolution for } N = 2 \text{ nuclei. Energy levels are marked. It shows the probability } P \text{ of arrival at an } LZ-LAC \text{ (boxed) and probabilities } P^{(1)} \text{ and } P^{(2)} \text{ of bifurcation right or down (traveling toward the } m_i = 0 \text{ and } m_i = +1 \text{ manifolds, respectively). Colored arrows represent contributions to the same nuclear state } S \text{ from different electronic manifolds, which are eventually combined due to the action of the laser [Eq. (C15)]. For example, the probability of ending in the } |11\rangle \text{ state (assuming unit value starting population) is } P_{11} = P_{11}^{(1)} + P_{11}^{(2)}. \text{ Contributing populations from both electronic manifolds, } P_{11}^{(1)} \text{ and } P_{11}^{(2)} \text{, are highlighted by red arrows in this case.}\]
Taking identical $\eta_{i\ell}$ values for every energy gap $\varepsilon_{i\ell}$ gives the following simple expression:

$$p^{(2)} = \eta^{2s}(1 - \eta)^{6}.$$ 

This tractable method of tracking nuclear spin populations is the key result of this paper.

3. General traversal through the $I_{k\ell}$ checkerboard

Following from Eqs. (C10)–(C13), given a final coordinate in the $I_{k\ell}$ checkerboard, it is possible to retrospectively determine all paths that lead to it and, hence, the transfer probability as the sum over all the paths the system can traverse. Considering traversal from an initial coordinate $(k_i, \ell_i)$ to a final coordinate $(k_f, \ell_f)$, there are, in general, $(\ell_f - \ell_i)$ vertical steps and $(k_f - k_i)$ horizontal steps required. This gives rise to $L = (k_f + \ell_f - k_i - \ell_i)$ total traversal steps, and there are hence $L_p = \binom{L}{\ell_f, \ell_i}$ total paths of the traversal, where $(\cdot)$ is the binomial operator. Following Eq. (C12), we can write the traversal probability from $(k_i, \ell_i)$ to $(k_f, \ell_f)$ as

$$p[k_i, \ell_i \rightarrow k_f, \ell_f] = \sum_{\ell_i<\ell_f} \binom{L}{\ell_f, \ell_i} C_{\ell_f}. \tag{C14}$$

Equation (C14) generalizes finding traversal probabilities for any trajectory over vertices $v$, where the index $j$ represents the position on the path.

4. Electron repolarization: Action of laser

Key to the hyperpolarization process is the ability to regenerate the populations of the NV electrons by means of optical pumping. This permits the ability to repeatedly accumulate polarization in the nuclear spins using them to indirectly report on the ESR spectrum of the electrons. We assume that the action of the laser instantaneously affects nuclear spins using them to indirectly report on the ESR spectrum of the populations of the NV electrons by means of optical pumping.

APPENDIX D: GALTON BOARD HYPERPOLARIZATION

1. Calculating the nuclear polarization $P$

Elucidating the magnitude of polarization is essential to understanding the origin of nuclear polarization “bias” and is key to calculating traversal probability through the LZ Galton board. Using Eq. (C14), we can find the population at any final point $(k_f, \ell_f)$, which then permits finding the population of any nuclear state $S$ after traversal through an LZ cascade. Since each nuclear state appears once for each electronic manifold, the imbalance upon system traversal can be accounted for by evaluating the total population in each state at any time instant through the diagram. The population in the $m_i = 0$ state then takes the form [see Eq. (C2)]

$$p_{2N, \ell_f}^{(2)} \equiv \sum_{n=1}^{2N} p^{(2)}[(1, n) \rightarrow (2N, \ell_f)]. \tag{D1}$$

where the sum indicates the total probability starting from the left column of the diagram. Similarly, the population in the $m_i = +1$ state, assuming $A^l > 0$, takes the form

$$p_{2N, \ell_f}^{(2)} \equiv \sum_{n=1}^{2N} p^{(2)}[(1, n) \rightarrow (2N, \ell_f)]. \tag{D2}$$

Due to the action of the laser [Eq. (C15)], these populations are effectively merged and the population of any nuclear state $S$ is

$$P_n = p_{2N, \ell_f}^{(2)} + p_{2N, \ell_f}^{(2)} \tag{D3}$$

where the subscript $n \in \{1 \ldots 2N\}$ here indexes the state $S$ and the individual terms can be calculated according to Eq. (C14). For instance, this is schematically shown for the state $P_{14}$ in Fig. 9. Finally, the nuclear polarization $P$ is defined as the net excess of population in the nuclear down states compared to the up states, and for the case of $A^l > 0$ that we consider,

$$P = \sum_{n=1}^{2N} P_n - \sum_{n=2N+1}^{2N} P_n. \tag{D4}$$

2. Special case: Single-spin ratchet

As a simple application, consider an NV center coupled to a single $^{13}$C nuclear spin. The mechanism here was referred to as a “spin ratchet” in Ref. 23. We note that while this case ($N = 1$) was considered before in Ref. 38, the Galton board analogies in Fig. 10 provide a simple means to analyze the bifurcation and recombinations of the populations in an intuitive and graphical manner. The analogy also provides a means to generalize the mechanism of operation to larger $N$, an $a$ priori non-trivial problem that has not been previously considered elsewhere.
in the Galton board in Fig. 10(c). This provides us a method to calculate the individual probabilities as

$$P(\downarrow \rightarrow \downarrow) = (1 - \eta_{1,1}) + \eta_{1,2}\eta_{1,1},$$
$$P(\downarrow \rightarrow \uparrow) = \eta_{1,2}(1 - \eta_{1,1}),$$
$$P(\uparrow \rightarrow \downarrow) = \eta_{1,2}(1 - \eta_{1,1}) + 2\eta_{1,1}(1 - \eta_{1,1})(1 - \eta_{1,2}),$$
$$P(\uparrow \rightarrow \uparrow) = \eta_{1,1}\eta_{1,2} + \eta_{1,1}^2(1 - \eta_{1,2}) + (1 - \eta_{1,1})^2(1 - \eta_{1,2}),$$

where the tunneling probabilities follow Eq. (C3), and we have exploited symmetries in energy gaps (described in Appendix B 5). Each term in these expressions corresponds to a different trajectory through $I_{k,\ell}$. For instance, there are two paths that constitute the term $P(\downarrow \rightarrow \downarrow)$, corresponding to the probabilities of $|0, \downarrow \rangle \rightarrow |0, \downarrow \rangle$ and $|0, \downarrow \rangle \rightarrow |1, \downarrow \rangle$. This permits a means to determine the nuclear hyperpolarization, where we evaluate the difference in populations between the nuclear states at the end of the sweep as

$$P = \left[ P(\downarrow \rightarrow \downarrow) + P(\uparrow \rightarrow \uparrow) \right] - \left[ P(\downarrow \rightarrow \uparrow) + P(\uparrow \rightarrow \downarrow) \right] = (1 - \eta_{1,1})\left[1 - (2\eta_{1,1} - 1)^2\right]. \tag{D5}$$

Ultimately, the expression in Eq. (D5) demonstrates that the polarization levels are obtained as the difference of the probabilities of transitions to spin down states and transitions to spin up states.

It is simplest to evaluate Eq. (D5) for the situation when the Rabi frequency $\Omega_k$ is large so that the traversals through the energy gaps $\varepsilon_{1,2}$ and $\varepsilon_{2,1}$ are adiabatic, but those through the others are diabatic. We then have $P = 1 - (2\eta_{1,1} - 1)^2$; a non-zero hyperpolarization develops through an accumulation of nuclear spins in the $|\downarrow \rangle$ state with a single MW sweep. Building on Eq. (D5) then, the net hyperpolarization developed in a total time $T$ [Fig. 1(c)] is

$$P_{\text{net}} = \left[1 - \exp\left(-\frac{w_k}{f_r}\right)\right] \cdot T f_r \cdot \left[1 - (2\eta_{1,1} - 1)^2\right], \tag{D6}$$

where the first term encapsulates the starting electron polarization, the second term ($\propto T f_r$) gives the total sweeps in time $T$, and the last term is Eq. (D5). The mechanism can, therefore, be thought of as a "ratchet"—every MW sweep develops a finite amount of polarization.

(i) Case of $A^1 > 0$: Consider a single traversal from left-to-right starting from populations restricted to the $m_i = 0$ manifold and ending with NV repolarization. Using Eq. (D3) and following Eq. (C14), the probability of the nuclear state $|\downarrow \rangle$ remaining in $|\downarrow \rangle$ can be written as

$$P(\downarrow \rightarrow \downarrow) = p_{2,2}^+(1) + p_{1,2}^+(2),$$

taking

$$p_{2,2}^+(1) = P^{(1)}[(1,2) \rightarrow (2,2)]$$
$$p_{1,2}^+(2) = P^{(3)}[(1,2)].$$

In Fig. 10, we consider both cases of hyperfine coupling $A^1 > 0$ [Fig. 10(a)] and $A^1 < 0$ [Fig. 10(b)], with Figs. 10(c) and 10(d) showing the corresponding $I_{k,\ell}$ checkerboards. Apart from the reversed order of levels in the $m_i = 0$ manifold, the structures in these diagrams are similar. This inversion arises from the difference in order in which the LZ-LACs corresponding to the "small" and "large" energy gaps are encountered during a MW sweep.

(ii) Case of $A^1 < 0$: A similar analysis can be carried out for the situation with $A^1 < 0$ [see Fig. 10(b)], yielding

$$P(\downarrow \rightarrow \downarrow) = \eta_{1,1}\eta_{1,2} + \eta_{1,2}(1 - \eta_{1,1}),$$
$$P(\downarrow \rightarrow \uparrow) = (1 - \eta_{1,2}),$$
$$P(\uparrow \rightarrow \downarrow) = (1 - \eta_{1,1})^2(1 - \eta_{1,2}) + \eta_{1,1}^2(1 - \eta_{1,2}) + 2\eta_{1,1}(1 - \eta_{1,1})(1 - \eta_{1,2}),$$
$$P(\uparrow \rightarrow \uparrow) = \eta_{1,1}\eta_{1,2} + \eta_{1,2}(1 - \eta_{1,1}).$$
once again exploiting symmetrical energy gaps. The polarization developed upon one MW sweep [similar to Eq. (D5)] now gives

\[
P = [P(\downarrow \rightarrow \downarrow) + P(\uparrow \rightarrow \downarrow)] - [P(\downarrow \rightarrow \uparrow) + P(\uparrow \rightarrow \uparrow)] = 0.
\]

(D7)

There is, therefore, no net buildup of polarization in this case, a consequence of a fine balance between the population traversals in the two arms of the Galton board in Fig. 10(b).

(iii) Sweep direction dependence: The discussion above is centered on low-to-high frequency sweeps for the two cases of positive and negative hyperfine coupling. Consider now the opposite scenario to Figs. 10(a) and 10(b), where sweeps are applied from high-to-low frequency. The order of the two energy gaps in (i) and (ii) is now reversed. This results in (i) no effective hyperpolarization in the \(A^\parallel > 0\) case and (ii) hyperpolarization in the \(|\uparrow\rangle\) state in the \(A^\parallel < 0\) case. The expressions are identical to that in Eq. (D5). We note that this results in two consequences that are borne out by experiments (see the main paper).

(1) Due to equal proportions of \(A^\parallel < 0\) and \(A^\parallel > 0\) present in experiments, there is an inversion in the hyperpolarization sign upon a reversal in the direction of the MW sweep. This is in contrast with other DNP methods (e.g., solid effect) where the DNP sign is different for the two halves of the spectrum.

(2) A consequence is that all parts of the spectrum yield the same sign in the \(^{13}\)C hyperpolarization signal, making unraveling the underlying electronic spectrum a simpler experimental undertaking.

(3) Finally, in the case of large \(N\) systems, one would expect a slight shift in the frequency center of the DNP derived spectrum in the case of one sweep direction with respect to the other.

**FIG. 11.** Evolution of nuclear populations through the LZ Galton board. Panels show the emergence of nuclear hyperpolarization upon a low-to-high frequency MW sweep (assuming \(\eta_{k,2} N = 0\) along the conjugate diagonal). (a) LZ cascade for \(N = 3\) nuclei (shown in the inset) and \(A^\parallel > 0\) as in Fig. 7(d). (b) Traversal through LZ cascade. We extract the LZ-LAC points (red) in (a) to define the LZ Galton board (dashed lines). Representative nuclear states are marked. Panels show the evolution of nuclear populations (colored points), starting from different nuclear states \(S\) (indexed by \(n\) in a Hamming notation) in the \(m_s = 0\) manifold, under a MW sweep. Opacity of dots represents relative population. There is a clear bias toward nuclear down states. (c) Population bias and emergence of hyperpolarization. Final populations in different nuclear states (numbered in a Hamming ordering) in the \(m_s = 0\) and \(m_s = +1\) manifolds (blue and red points, respectively) after the traversals through the LZ Galton board shown in (b). The dashed line represents the hyperpolarization level. (d) Populations similar to (c), but for \(N = 4\). (e) Populations similar to (d), but now for \(A^\parallel < 0\). Due to the change in the order of energy levels and energy gaps, there is no net polarization developed [see also Fig. 10(d)].
3. Origin of nuclear polarization bias

The origin of hyperpolarization can be traced to the differential traversal through the $I_{kL}$ checkerboard in a manner that “biases” the system to increase population in particular nuclear states at the cost of others. Considering the example of an NV coupled to a single nuclear spin, Eq. (D5) shows a biased traversal that follows,

$$
p_f(\downarrow) = p_f(\downarrow) + \beta p_f(\uparrow), \quad p_f(\uparrow) = (1 - \beta)p_f(\downarrow),
$$

where $\beta$ is a finite probability and $p_f(\cdot)$ and $p_i(\cdot)$ refer to nuclear populations before and after traversal through the LZ Galton board and have the form

$$
p_i(\downarrow) = p_{i,2}(1), \quad p_i(\uparrow) = p_{i,1}(1),
$$

$$
p_f(\downarrow) = p_{f,2}(1) + p_{f,2}(2), \quad p_f(\uparrow) = p_{f,1}(1) + p_{f,2}(2).
$$

Effectively, one of the nuclear states (here $\downarrow$) is unaffected, while the other (here $\uparrow$) is flipped with the probability $\beta$. Successive sweeps through the LZ system then set up a “ratchet” that builds nuclear hyperpolarization in the $\downarrow$ state.

To understand the origin of this bias for larger $N$, consider traversal through the full checkerboard in Fig. 6. As we demonstrate in Fig. 11, a combined consequence of (i) the large energy gaps along the conjugate diagonal, (ii) the order that the energy gaps are encountered in, and (iii) the tilted nature of the LZ Galton board, there is a natural bias in evolution toward the left and bottom of the diagram (Fig. 11). This net excess of population in the nuclear down states over the nuclear up states [Eq. (D4)] ultimately yields hyperpolarization.

To traverse the Galton board, a Hamming ordering is used in Fig. 11(b) then show the populations of nuclear states at each point on the $I_{kL}$ checkerboard. Specifically, we consider the population levels at each energy gap in the ladder model in Fig. 11(a), the order of the nuclear states in the $m_n = 0$ manifold is reversed, and the large energy gaps appear on the diagonal instead of the conjugate diagonal. As a result, the development of polarization bias is impeded through a fine counterbalance of the nuclear populations as they traverse the Galton board. A type of destructive interference then ensues, resulting in no hyperpolarization in this case.

Finally, Fig. 11(f) considers the inverted scenario where $A\uparrow < 0$ for an identical Galton board and a full MW sweep is carried out. In this case, while the LZ cascade has a similar structure to the diagram in Fig. 11(a), the order of the nuclear states in the $m_n = +1$ manifold is reversed, and the large energy gaps appear on the diagonal instead of the conjugate diagonal. As a result, the development of polarization bias is impeded through a fine counterbalance of the nuclear populations as they traverse the Galton board. A type of destructive interference then ensues, resulting in no hyperpolarization in this case.

4. Analogy to Mach-Zehnder interferometry

We note finally that the Galton board illustrated in Figs. 10(c) and 10(d) bears resemblance to the construction of a Mach–Zehnder (MZ) interferometer, where the LZ-LACs serve analogous to beam splitters. One might then consider the fine cancellation occurring in Fig. 10(d) as an interference effect between the two arms of the MZ interferometer. A more detailed discussion of this connection is beyond the scope of this article; however, we note that such connections could elevate the LZ-LAC checkerboard, naturally occurring in spin systems as in Fig. 1 to applications exploiting the power of parallelized interferences in cascaded MZ interferometers (e.g., BosonSampling\textsuperscript{8}).

5. Numerical simulations

The formalism developed via Eqs. (C12), (C14), (D3), and (D4) permits for a tractable solution for the traversals through a LZ-Galton board. Before an analytical solution, we first consider a numerical evaluation in Fig. 11, considering the case of $N = 3$ and $A\uparrow > 0$—and assuming for simplicity $\theta = \pi/2$—with the LZ cascade structure shown in Fig. 11(a). We consider evolution under a low-to-high frequency MW sweep and solve the traversal following Eq. (D3). We assume that, as in experiments, the Rabi frequency $\Omega_f$ is large such that the energy gaps at the conjugate diagonals are large and traversals through them are adiabatic. The individual panels in Fig. 11(b) then show the populations of nuclear states at each point on the $I_{kL}$ checkerboard, starting with populations confined to starting $m = 0$ nuclear states $S$ (indexed by $n$). We track the populations (dots) after each of the $I_{kL}$ LZ-LACs (red points), where the opacity of the dots denotes the normalized population level. The analogy to the classical Galton board is evident here [Fig. 4(c)]; there is a “sieving” effect as the populations bifurcate at each LZ-LAC, yielding progressively smaller populations as one traverses deeper into the checkerboard. There is an intrinsic bias toward the left and bottom of the Galton board [evident in Fig. 11(b)]; this ultimately yields hyperpolarization.

Figure 11(c) makes this more clear by plotting the resulting nuclear state populations in the $m_n = 0$ and $m_n = +1$ manifolds (blue and red points, respectively) following a sweep over the full Galton board. Figure 11(d) shows an analogous calculation for $N = 4$. Representative nuclear states are marked, and state $n$ follows a Hamming ordering. In Figs. 11(c) and 11(d), a decrease in population is evident with increasing state number $n$ in each manifold, while the population of a particular nuclear state is higher in the $m_n = +1$ (red) manifold than in the $m_n = 0$ (blue) one. Both these observations reflect the bias in the Galton board traversal. Ultimately, upon application of the laser to repolarize all the electronic polarization to $m_n = 0$, one obtains nuclear hyperpolarization, the value of which is denoted by the black dashed lines in Figs. 11(c) and 11(d).

Finally, Fig. 11(f) consider the inverted scenario where $A\uparrow < 0$ (for an identical Galton board) and a full MW sweep is carried out. In this case, while the LZ cascade has a similar structure to the diagram in Fig. 11(a), the order of the nuclear states in the $m_n = +1$ manifold is reversed, and the large energy gaps appear on the diagonal instead of the conjugate diagonal. As a result, the development of polarization bias is impeded through a fine counterbalance of the nuclear populations as they traverse the Galton board. A type of destructive interference then ensues, resulting in no hyperpolarization in this case. This is shown in Fig. 11(e), where we consider the populations in each of the nuclear states similar to Figs. 11(c) and 11(d), assuming that the diagonal energy gaps are large so that traversals through them are adiabatic. All the nuclear states in each manifold then have the same population, and there is no net development of hyperpolarization. We note, however, that the situations for $A\uparrow > 0$ and $A\uparrow < 0$ are exactly reversed when the MW sweep is applied from high-to-low frequency.

6. Theoretical evaluation of Galton board traversal

The numerical solution to traversals through an LZ Galton board in Fig. 11, while revealing the essential physics of the biased traversal and buildup of hyperpolarization, is still unwieldy to solve for large $N$. This is because of the exponentially scaling number of LZ-LACs the system entails ($\approx 2^{20N}$). That said, however, the analogy to the classical Galton board developed above [see Figs. 4(b) and 4(c)] makes feasible a full analytic solution under certain simplifying assumptions. Consider first that the initial nuclear populations are equally distributed among states in the $m_n = 0$ electronic manifold before entering the LZ Galton board at points $(1, \ell)$. Nuclear
populations travel along horizontal lines \( \ell \) and vertical lines \( k \) in the LZ Galton board and redistribute at every LZ-LAC on \( \mathcal{L}_{\ell,k} \), where \( k, \ell \in 1 \ldots 2^N \). Similar to the assumptions made in a classical Galton board, we define the probability of redistribution down and right to be \( p \) and \( q \), respectively, at every LZ-LAC, with \( p + q = 1 \). In addition, for points along the conjugate diagonal, we assume that the energy gaps are large enough that \( \eta_{n} 2^\ell k 2^\ell = 0 \), and thus, traversals are adiabatic. We demonstrate below that these assumptions permit us to capture the physics of the cascaded LZ-LAC traversal while permitting an analytical solution (Fig. 12).

Toward this end, we evaluate the Galton board traversal to determine the probability of the total nuclear population that ends up in each specific spin state \( \mathcal{S} \), indexed by \( n \) (where \( n = 1 \ldots 2^N \)). Due to the action of the laser [Eq. (G15)], the nuclear population in any state \( n \) is then just the sum of the population that exits point \( (n, 2^N) \) downward and point \( (2^N, 2^N - n + 1) \) to the right [as described in Eq. (D3)].

We first consider the traversal of a nuclear population starting at a point \( (1, \ell) \) before cascading through the board. The population entering at point \( (1, \ell) \) will necessarily travel down due to the large energy gap it immediately encounters. We can express this with a function \( c(n) \), which is equal to 1 when \( n = 1 \) and is equal to 0 otherwise.

For nuclear populations starting at any other \( \ell \in 1 \ldots 2^N - 1 \), we can now employ logic similar to that in a classical Galton board to evaluate the probabilities of each spin state. For states ending in the \( m_0 = +1 \) manifold, any nuclear population must travel \( 2^N - \ell - 1 \) steps down and \( n - 2 \) steps right (disregarding movement through the conjugate diagonal). Because the nuclear population can take a variety of trajectories (e.g., Fig. 6) to reach the spin state, we can use a combinatoric to find the number of ways to choose \( n - 2 \) right steps from the total steps. Thus, we can write the probability as the exact form \([1_{\ell} + 2\ell_{\ell-1}]\) \( p^{2^N-\ell} q^{n-2} \), where \( 1_{\ell} \) is a combinatoric operator, revealing a binomial form similar to a classical Galton board. Likewise, we can compute the probability for reaching a spin state \( n \) on the right (in the \( m_0 = 0 \) manifold), which requires \( 2^N - n - \ell \) down steps and \( 2^N - 2 \) right steps. This probability is written as \([1_{\ell} + 2\ell_{\ell-1}]\) \( p^{2^N-n-\ell} q^{N-n-2} \). Combining both results, we can write the total probability that a nuclear population from a point \( (1, \ell) \), where \( \ell = 1 \ldots 2^N - 1 \), will end up in a specific spin state \( n \) as

\[
P_{n,\ell} = \binom{n-2}{n-2} \binom{2^N-\ell-1}{n-2} p^{2^N-\ell} q^{n-2} + \binom{2^N-n-\ell}{2^N-n-\ell} p^{2^N-n-\ell} q^{n-2},
\]

where \( p_{n,\ell} \) is the same probability as in Eq. (D3).

Figure 12 displays the result of this analytic expression [Eq. (D10)] for a LZ Galton board of sizes \( N = 4 \) and \( N = 8 \). We emphasize the strong resemblance to the numerical simulations in Figs. 11(c) and 11(d). This also illustrates that the essential physics of the LZ Galton traversal and the development of hyperpolarization are less affected by the exact energy gaps at the individual LZ-LACs.

Interesting to note is the case of the reverse sweep (high-to-low frequency), in which the population starts from the right side of the Galton board and traverses through the board by moving either up or left at each LZ-LAC with probabilities \( p \) and \( q \). Because this is the same board and all other above assumptions apply, it becomes clear that there is symmetry between the two cases. Specifically, the reverse sweep is identical in behavior to the original sweep when the board is flipped across the conjugate diagonal. This means that we can use the same analytical solutions we have acquired for the original sweep to the reverse sweep, with a relabeling of the states as \( s \) according to the symmetrical flip (where \( s = 2^N - n \)). This takes the form

\[
P_{s} = \frac{1}{2^N} \sum_{s=1}^{2^N-1} \binom{2^N-s-2}{s-2} p^{2^N-s-2} q^{s-2} + \binom{(s-\ell) + (2^N-2)}{s-\ell} p^{s-\ell} q^{2^N-s-1} + c(2^N-s).
\]

An evaluation of Eq. (D11) then shows, by symmetry, the development of opposite polarization in this case, matching experimental results [Fig. 2(h)].

7. Evaluation of a window sweep on the Galton board

While Sec. II explores the dynamics of a full sweep of the Galton board, we now turn our focus to the case when a small window \( B \) is swept (corresponding to experiments in Fig. 2). Analytic solutions similar to Eq. (C14) are still tractable, but due to expressions being considerably more complex than the full sweep behavior, here, we instead carry out a numerical solution. We employ the same assumptions above that each LZ-LAC is encountered sequentially and that
the energy gaps along the conjugate diagonal are large. First, motivated by experiment, we assume a Gaussian distribution for energy levels (DOS) in the $m_s = +1$ manifold, as seen in Fig. 13(a). This modulates the spacing of the $I_{k,\ell}$ columns and impacts the number of $m_s = +1$ energy levels that are swept in any specific frequency window $\mathcal{B}$.

We employ a physically motivated method of evaluating traversals through the board. First, note that the ability to uncover spectral DOS mapping dynamics necessarily requires simulations of large $N$ Galton boards to prevent artifacts stemming from edge effects in small $N$ systems. For large Galton boards as in Fig. 13(a) (which is for $N = 8$ nuclei, thus having 256 nuclear states), however, the full simulation approach employed in Fig. 11 proves expensive and unwieldy due to the exponential scaling system size. Instead, here, for simplicity, we choose a specific order in which the LZ-LACs are evaluated—solving the result of traversals through each $I_{k,\ell}$ column from the top to the bottom, working through the board from left to right. This is an acceptable assumption because the bifurcation action at any LZ-LAC is only dependent on previously encountered LZ-LACs above or to the left of it. With this additional assumption in place, we can evaluate the traversals of populations, starting and ending within a specified window $\mathcal{B}$ defined by its starting column and width. We choose a large Galton board ($N = 8$) in Fig. 13(a), and since evaluations are column-wise here, we show the board without its tilt.

Following this approach, Fig. 13(b) shows the numerical evaluations of the traversal of the board in Fig. 13(a) with varying $\mathcal{B}$ and both forward (dark) and reverse (light) sweeps. These plots are produced by taking repeated window sweeps of a set size $\mathcal{B}$ while gradually moving the starting point [corresponding to the starting point $f_0$ in Fig. 2(a)] through the board and calculating the polarization after the population in each state has redistributed following Eq. (C14). With the increasing window size [e.g., in Figs. 13(b-ii) and 13(b-iii)], we observe that the obtained hyperpolarization profiles approximately trace the underlying electronic DOS of the underlying LZ Galton board, in this case the Gaussian function chosen. There is also an increase in overall polarization as the window size $\mathcal{B}$ increases and an increasing width in the hyperpolarization profile with increasing $\mathcal{B}$ [see Fig. 13(b)]. Both these features match experimental observations (Fig. 2).

Why does the observed hyperpolarization signal approximately track the electronic spectral DOS? Insights into this are revealed in Figs. 13(b-i) and 13(c). For narrow window sizes $\mathcal{B}$, the simulations in Fig. 13(b-i) reveal that one half of the Galton board produces positive nuclear polarization, while the other half produces no net polarization. Moving from left-to-right in Fig. 13(b-i), for instance, we identify three regimes in the obtained hyperpolarization profiles: regime $\circlearrowright$, in which there is an increase in polarization; regime $\circlearrowleft$, in which there is a linear decrease; and regime $\bullet$ with zero net polarization. As the window size $\mathcal{B}$ increases, the differences in the profiles between the three regimes become less prominent, and ultimately, in Fig. 13(c-iii), the profile appears Gaussian-like. At this point, the profiles approximate the underlying spectral DOS in the starting LZ Galton board.

To unravel the internal dynamics of the Galton traversals that yield Fig. 13(b), let us start by considering a representative sweep in regime $\circlearrowright$ of Fig. 13(b-i). The result is shown in Fig. 13(c-i), where we plot the nuclear populations in each of the $2^N$ levels (labeled $n$) after

---

**FIG. 13.** Numerical simulation showing “ESR-via-NMR” spectral mapping. (a) Lower panel shows an exemplary LZ Galton board with $N = 8$ nuclei employed in simulations. Energy levels in the $m_s = +1$ manifold have a Gaussian DOS of width =13.5 MHz (upper panel) similar to Fig. 1(b). Units chosen here for the Galton board extent are arbitrary and just used for illustration. Since numerical evaluation is performed column-wise, the tilt of the Galton board is not shown here. (b) Numerical result showing the developed $^{13}$C hyperpolarization using sweep windows of size $\mathcal{B}$ of increasing size through the Galton board in (a), similar to the experiments in Fig. 2. Forward (dark) and reverse (light) sweeps result in positive and negative polarization, respectively. Increasing $\mathcal{B}$ yields a greater hyperpolarization signal and a broader spectral profile, matching experimental observations (Fig. 2). For narrow $\mathcal{B}$ (b-i), we find three distinct regimes in the hyperpolarization profiles (circled), where there is a sharp increase, a rapid linear decrease, and no net polarization, respectively. With increasing $\mathcal{B}$, the profiles begin to approximate the DOS profile of the underlying Galton board being swept over. (c) Unraveling the origin of the hyperpolarization profile in (b-i). Representative nuclear states are marked. For each of the three regimes, we plot the resulting nuclear populations in the $2^8 = 256$ nuclear states, numbered $n$ following a Hamming convention. Hyperpolarization is evaluated as the difference in populations between two halves of this plot (indicated by the dashed line), following Eq. (D4): In regime 1 (c-i), there is an emergence of hyperpolarization because the population imbalances constructively add. In regime 3 (c-iii), however, the population imbalances are in the same half of the plot, yielding no net polarization.
the sweep over $B$ is completed. In this regime, it is predominantly the net nuclear-down states that are being swept over. A (positive) increase in the nuclear populations is then evident in nuclear states that are being swept over; this arises from the populations effectively moving toward the bottom of the LZ-Galton board. Similarly, there is a decrease of populations in high-$n$ nuclear states, corresponding to predominantly nuclear up states. Since the final polarization plotted in Fig. 13(b-i) is evaluated [following Eq. (D4)] as the difference in populations between the nuclear states on either half of the plot in Fig. 13(c-i) (denoted by the dashed line), there is a net development of hyperpolarization in this case. Indeed, Fig. 13(c-i) suggests that the polarization produced is approximately proportional to the number of levels swept over since the “positive” portion of this population imbalance has a width that scales with $B$.

In a similar manner, Fig. 13(c-ii) shows a sweep over a window $B$ that contains a mix of net nuclear-down and up states (regime $\circlearrowleft$). In this case, the positive and negative population regions move closer together [see Fig. 13(c-ii)]. A difference (across the dashed line) then occurs in the half of the plot; hence, there is no hyperpolarization buildup. Ultimately, a combination of these features yields the profile in Fig. 13(b-ii). It is illustrative that the reverse sweep [light line in Fig. 13(b-i)] has a mirr or-inverted profile about the Galton board center. Finally, upon increasing $B$ [Figs. 13(b-ii) and 13(b-iii)], the sharp differences between the three regimes in Fig. 13(b-i) become less prominent since the profile becomes a convolution with the (larger) sweep window. In this case, both positive and negative sweeps yield profiles that approximately map the spectral DOS.

REFERENCES

1. C. Arenz, G. Guidali, and D. Burghart, “Control of open quantum systems: Case study of the central spin model,” New J. Phys. 16, 065023 (2014).

2. M. Witzel, M. S. Carroll, A. Morello, L. Gwyinski, and S. Das Sarma, “Electron spin decoherence in isotope-enriched silicon,” Phys. Rev. Lett. 105, 187602 (2010).

3. C. L. Degen, F. Reinhard, and P. Cappellaro, “Quantum sensing,” Rev. Mod. Phys. 89, 035002 (2017).

4. T. H. Taminiau, J. J. T. Wagenaar, T. van der Sar, F. Jelezko, V. V. Dobroviskii, and R. Hanson, “Detection and control of individual nuclear spins using a weakly coupled electron spin,” Phys. Rev. Lett. 109, 137602 (2012).

5. Y. Hovav, A. Feintuch, and S. Vega, “Theoretical aspects of dynamic nuclear polarization in the solid state—the solid effect,” J. Magn. Reson. 214, 29 (2012).

6. A. Morello, J. J. Pla, F. A. Zwanenburg, K. W. Chan, K. Y. Tan, H. Hübli, M. Mottonen, C. D. Nugroho, C. Yang, J. A. van Donkelaar, A. D. C. Alves, D. N. Jamieson, C. C. Escott, L. C. L. Hollenberg, R. G. Clark, and A. S. Dzurak, “Single-shot readout of an electron spin in silicon,” Nature 467, 687 (2010).

7. J. J. Pla, K. Y. Tan, J. P. Dehollain, W. H. Lim, J. J. Morton, D. N. Jamieson, A. S. Dzurak, and A. Morello, “A single-atom electron spin qubit in silicon,” Nature 489, 541 (2012).

8. F. Jelezko and J. Wrachtrup, “Single defect centres in diamond: A review,” Phys. Status Solidi A 203, 3207 (2006).

9. M. Taylor, P. Cappellaro, L. Childress, L. Jiang, D. Budker, P. R. Hemmer, A. Yacoby, R. Walsworth, and M. D. Lukin, “High-sensitivity diamond magnetometer with nanoscale resolution,” Nat. Phys. 4, 810 (2008).

10. T. Maly, G. T. Debelouchina, V. S. Bajaj, K.-N. Hu, C.-G. Joe, M. L. Malikurkaskas, J. R. Sirigiri, P. C. A. van der Wel, J. Herzfeld, R. J. Temkin, and R. G. Griffin, “Dynamic nuclear polarization at high magnetic fields,” J. Chem. Phys. 138, 052521 (2008).

11. K.-N. Hu, V. S. Bajaj, M. Rosay, and R. G. Griffin, “High-frequency dynamic nuclear polarization using mixtures of tempo and trityl radicals,” J. Chem. Phys. 126, 044512 (2007).

12. F. Jelezko, T. Gaebel, I. Popa, M. Domhan, A. Gruber, and J. Wrachtrup, “Observation of coherent oscillation of a single nuclear spin and realization of a two-qubit conditional quantum gate,” Phys. Rev. Lett. 93, 130501 (2004).

13. N. B. Manson, J. P. Harrison, and M. J. Sellars, “Nitrogen-vacancy center in diamond: Model of the electronic structure and associated dynamics,” Phys. Rev. B 74, 104303 (2006).

14. A. Gali, M. Fytta, and E. Kaxiras, “Ab initio supercell calculations on nitrogen-vacancy center in diamond: Electronic structure and hyperfine tensors,” Phys. Rev. B 77, 155206 (2008).

15. L. M. Pham, D. Le Sage, P. L. Stanwix, T. K. Yeung, D. Glenn, A. Trifonov, P. Cappellaro, P. R. Hemmer, M. D. Lukin, H. Park, A. Yacoby, and R. L. Walsworth, “Magnetic field imaging with nitrogen-vacancy ensembles,” New J. Phys. 13, 045021 (2011).

16. J. F. Barry, J. M. Schloss, E. Bauch, M. J. Turner, C. A. Hart, L. M. Pham, and R. L. Walsworth, “Sensitivity optimization for NV-diamond magnetometry,” Rev. Mod. Phys. 92, 015004 (2020).

17. J.-P. Tettenne, L. Rondin, P. Spinicelli, M. Chipaux, T. Debuischert, J.-F. Roch, and V. Jacques, “Magnetic-field-dependent photodynamics of single NV defects in diamond: An application to qualitative all-optical magnetic imaging,” New J. Phys. 14, 103033 (2012).

18. L. Rondin, J.-P. Tettenne, T. Hingant, J.-F. Roch, P. Maletinsky, and V. Jacques, “Magnetometry with nitrogen-vacancy defects in diamond,” Rep. Prog. Phys. 77, 056503 (2014).

19. D. Le Sage, L. M. Pham, N. Bar-Gill, C. Beltangady, M. D. Lukin, A. Yacoby, and R. L. Walsworth, “Efficient photon detection from color centers in a diamond optical waveguide,” Phys. Rev. B 85, 121202 (2012).

20. B. J. Shields, Q. P. Unterreithmeier, N. P. De Leon, H. Park, and M. D. Lukin, “Efficient readout of a single spin state in diamond via spin-to-charge conversion,” Phys. Rev. Lett. 114, 136402 (2015).

21. P. Siyushev, M. Nesladek, E. Bourgeois, M. Gulkja, J. Hruby, T. Yamamoto, M. Trupke, T. Teraji, J. Isoya, and F. Jelezko, “Photoelectrical imaging and coherent spin-state readout of single nitrogen-vacancy centers in diamond,” Science 363, 728 (2019).

22. A. Ajoy, K. Liu, R. Nazaryan, X. Lv, P. R. Zangara, B. Safvat, G. Wang, D. Arnold, G. Li, A. Lin et al., “Orientation-independent room temperature optical 13C hyperpolarization in powdered diamond,” Sci. Adv. 4, eaar5492 (2018).

23. A. Ajoy, R. Nazaryan, K. Liu, X. Lv, R. Safvat, G. Wang, E. Druga, J. Reimer, D. Suter, C. Ramanathan, C. A. Meriles, and A. Pines, “Enhanced dynamic nuclear polarization via swept microwave frequency combs,” Proc. Natl. Acad. Sci. U. S. A. 115, 10576 (2018).

24. W. Bestor, N. D. Janes, O. Akkiraju, A. Pillai, A. Oddo, P. Reshetikhin, E. Druga, M. McAllister, M. Elo, B. Gilbert et al., “Floquet prethermalization with lifetime exceeding 90s in a bulk hyperpolarized solid,” Phys. Rev. Lett. 127, 170603 (2021).

25. X. Lv, J. H. Walton, E. Druga, F. Wang, A. Aguilar, T. McKnelly, R. Nazaryan, F. L. Liu, W. O. Shenderova, D. B. Vigneron, C. A. Meriles, J. Reimer, A. Pines, and A. Ajoy, “Background-free dual-mode optical and 13C magnetic resonance imaging in diamond particles,” Proc. Natl. Acad. Sci. U. S. A. 118, 2023579113 (2021).

26. M. J. Jaroszewicz, A. R. Altenhof, R. W. Schurko, and L. Frydman, “Sensitivity enhancement by progressive saturation of the proton reservoir: A solid-state NMR analogue of chemical exchange saturation transfer,” J. Am. Chem. Soc. 143, 19778 (2021).

27. F. V. Can, J. J. Walsh, T. M. Swager, and R. G. Griffin, “Time domain DNP with the NOVEL sequence,” J. Chem. Phys. 143, 054201 (2015).

28. W. Becerra, G. J. Gerfen, R. J. Temkin, D. J. Singel, and R. G. Griffin, “Dynamic nuclear polarization with a cyclotron resonance maser at 5 T,” Phys. Rev. Lett. 71, 3561 (1993).

29. F. Mentink-Vijgier, S. Vega, and G. De Paep, “Fast and accurate MAS–DNP simulations of large spin ensembles,” Phys. Chem. Chem. Phys. 19, 3506 (2017).
L. Frydman, “Bulk nuclear polarization enhanced at room temperature by optical spin polarization in diamond,” Phys. Rev. B 97, 115213 (2018).

A. Abril, N. Aslam, A. Parker, J. King, C. E. Avalos, A. Ajoy, J. Wrachtrup, A. A. Meriles, and J. P. Woerdman, “Optical Galton board,” Phys. Rev. A 61, 031410 (1999).

N. Chernov and D. Dolgopyat, “Diffusive motion and recurrence on an idealized Galton board,” Phys. Rev. Lett. 99, 030601 (2007).

A. Pines, “Room temperature ‘optical nanodiamond hyperpolarizer Oon,” B. Safvati, R. Tsang, J. H. Walton, D. Suter, C. A. Meriles, J. A. Reimer, and J. A. Reimer, “Dynamics of frequency-swept nuclear polarization,” Phys. Rev. B 96, 030303 (2017).

A. J. Parker, K. Jeong, C. E. Avalos, B. J. M. Hausmann, C. C. Vassiliou, S. Abel, and A. Aguilar, B. Safvati, R. Nazaryan, J. T. Oon, B. Han, P. Raghavan, R. Nirodi, A. Aguilar, K. Liu, X. Cai et al., “Hyperpolarized relaxometry based nuclear polarization,” Phys. Rev. Lett. 119, 051001 (2017).

A. J. Parker, B. Safvati, R. Nazaryan, D. Suter, J. A. Reimer, A. Pines, and C. A. Meriles, “Dynamics of frequency-swept nuclear spin optical pumping in powdered diamond at low magnetic fields,” Proc. Natl. Acad. Sci. U. S. A. 116, 2521 (2019).

R. Fischer, C. O. Bretschneider, P. London, D. Budker, D. Gershoni, and D. Gershoni, “Evolution-free Hamiltonian parameter estimation and C nuclear spin in diamond,” Phys. Rev. B 94, 060101 (2016).

A. Ajoy, B. Safvati, R. Nazaryan, J. T. Oon, B. Han, P. Raghavan, R. Nirodi, A. Aguilar, K. Liu, X. Cai et al., “Hyperpolarized relaxometry based nuclear noise spectroscopy in diamond,” Nat. Commun. 6, 10520 (2015).

B. Wunderlich, J. Kohlrautz, B. Abel, J. Haase, and J. Meier, “Optically induced cross relaxation via nitrogen-related defects for bulk 13C hyperpolarization,” Phys. Rev. B 96, 220407 (2017).

V. K. Rhim, D. D. Elleman, J. B. Smith, P. G. R. Smith, and I. A. Walmsley, “Boson sampling on a photonic chip,” Science 366, 798 (2019).

J. Baum, M. Munowitz, A. N. Garroway, and A. Pines, “Multiple-quantum dynamics in solid state NMR,” J. Chem. Phys. 83, 195 (1985).

G. Boutis, D. Greenbaum, H. Cho, D. Cory, and C. Ramanathan, “Spin diffusion of correlated two-spin states in a dielectric crystal,” Phys. Rev. Lett. 92, 137201 (2004).

A. Ajoy, R. K. Rao, A. Kumar, and P. Rungta, “Algorithmic approach to simulate Hamiltonian dynamics and an NMR simulation of quantum state transfer,” Phys. Rev. A 85, 050303 (2012).

D. Burgarth and A. Ajoy, “Evolution-free Hamiltonian parameter estimation through Zeeman markers,” Phys. Rev. Lett. 119, 030402 (2017).

H. G. Krojanski and D. Suter, “Scaling of decoherence in wide NMR quantum registers,” Phys. Rev. Lett. 93, 090501 (2004).

B. Swingle, G. Bentsen, M. Schierer-Smith, and P. Hayden, “Measuring the scrambling of quantum information,” Phys. Rev. A 94, 040302 (2016).

S. Aaronson and A. Arkhipov, “The computational complexity of linear optics,” in Proceedings of the Forty-Third Annual ACM Symposium on Theory of Computing (2011), pp. 333–342.

M. Tillmann, B. Dakić, R. Heilmann, S. Nolte, A. Szameit, and P. Walther, “Experimental boson sampling,” Nat. Photonics 7, 540 (2013).

J. B. Spring, B. I. Mетal, P. C. Humphreys, W. S. Kolthammer, X.-M. Jin, M. Barbieri, A. Datta, N. Thomas-Peter, N. K. Langford, D. Kunits, J. C. Gates, B. J. Smith, P. G. R. Smith, and I. A. Walmsley, “Boson sampling on a photonic chip,” Science 339, 798 (2013).

H. Wang, Y. He, Y.-H. Li, Z.-E. Su, B. Li, H.-L. Huang, X. Ding, M.-C. Chen, C. Liu, J. Qin, J.-P. Li, Y.-M. He, C. Schneider, M. Kamp, C.-Z. Peng, S. Höfling, C.-Y. Lu, and J.-W. Pan, “High-efficiency multiphoton boson sampling,” Nat. Photonics 11, 361 (2017).

W. T. Wenckebach, “Dynamic nuclear polarization via thermal mixing: Beyond the high temperature approximation,” J. Magn. Reson. 277, 68 (2017).

J. Henshaw, D. Pagliero, P. R. Zangara, M. B. Franzoni, A. Ajoy, R. H. Acosta, J. A. Reimer, A. Pines, and C. A. Meriles, “Carbon-13 dynamic nuclear polarization in diamond via a microwave-free integrated cross effect,” Proc. Natl. Acad. Sci. U. S. A. 116, 18334 (2019).

F. Mentink-Vigier, U. Akbery, Y. Hovav, S. Vega, H. Oschkinat, and A. Feintuch, “Fast passage dynamic nuclear polarization on rotating solids,” J. Magn. Reson. 224, 13 (2012).
76 A. N. Pravdivtsev, A. V. Yurkovskaya, H.-M. Vieth, and K. L. Ivanov, “Spin mixing at level anti-crossings in the rotating frame makes high-field SABRE feasible,” Phys. Chem. Chem. Phys. 16, 24672 (2014).
77 A. N. Pravdivtsev, A. V. Yurkovskaya, H.-M. Vieth, and K. L. Ivanov, “RF-SABRE: A way to continuous spin hyperpolarization at high magnetic fields,” J. Phys. Chem. B 119, 13619 (2015).
78 A. Schliesser, R. Rivière, G. Anetsberger, O. Arcizet, and T. J. Kippenberg, "Resolved-sideband cooling of a micromechanical oscillator," Nat. Phys. 4, 415 (2008).
79 S. E. Hamann, D. L. Haycock, G. Klose, P. H. Pax, I. H. Deutsch, and P. S. Jessen, "Resolved-sideband Raman cooling to the ground state of an optical lattice," Phys. Rev. Lett. 80, 4149 (1998).
80 J. D. Teufel, T. Donner, D. Li, J. W. Harlow, M. S. Allman, K. Cicak, A. J. Sirois, J. D. Whittaker, K. W. Lehnert, and R. W. Simmonds, "Sideband cooling of micromechanical motion to the quantum ground state," Nature 475, 359 (2011).
81 D. Pagliero, P. R. Zangara, J. Henshaw, A. Ajoy, R. H. Acosta, J. A. Reimer, A. Pines, and C. A. Meriles, “Optically pumped spin polarization as a probe of many-body thermalization,” Sci. Adv. 6, eaaz6986 (2020).
82 D. Pagliero, P. R. Zangara, J. Henshaw, A. Ajoy, R. H. Acosta, N. Manson, J. A. Reimer, A. Pines, and C. A. Meriles, “Magnetic field induced delocalization in hybrid electron-nuclear spin ensembles,” Phys. Rev. B 103, 064310 (2021).
83 P. Millington-Hotze, S. Manna, S. F. Covre da Silva, A. Rastelli, and E. A. Chekhovich, "Nuclear spin diffusion in the central spin system of a GaAs/AlGaAs quantum dot," Nat. Commun. 14, 2677 (2023).
84 A. Henstra, P. Dirksen, and W. T. Wenckebach, "Enhanced dynamic nuclear polarization by the integrated solid effect," Phys. Lett. A 134, 134 (1988).
85 K. P. Zetie, S. F. Adams, and R. M. Tocknell, “How does a Mach-Zehnder interferometer work?,” Phys. Educ. 35, 46 (2000).
86 S. Aaronson and D. Gottesman, “Improved simulation of stabilizer circuits,” Phys. Rev. A 70, 052328 (2004).