Switched control of electron nuclear spin systems

Navin Khaneja*
Division of Engineering and Applied Science, Harvard University, 33 Oxford Street, Cambridge, Massachusetts 02138, USA
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We study control of electron-nuclear spin dynamics at magnetic field strengths where the Larmor frequency of the nucleus is comparable to the hyperfine coupling strength. The quantization axis for the nuclear spin differs from the static B_0 field direction and depends on the state of the electron spin. The quantization axis can be switched by flipping the state of electron spin, allowing for universal control of nuclear spin states. We show that by performing a sequence of flips (each followed by a suitable delay), we can perform any desired rotation of the nuclear spin, which can also be conditioned on the state of the electron spin. These operations, combined with electron spin rotations, can be used to synthesize any unitary transformation of the coupled electron-nuclear spin system. We discuss how these methods can be used for design of experiments for transfer of polarization from the electron to the nuclear spins.

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I. INTRODUCTION

In this paper, we study the problem of control of coupled electron-nuclear spin systems consisting of an electron, coupled with one or more nuclear spins. Manipulation of such electron-nuclear spin systems is fundamental in the field of electron spin resonance (ESR) and electron paramagnetic resonance (EPR) [1] with application to the study of the structure and dynamics of paramagnetic species. Coupled electron-nuclear spin systems have recently been explored as model systems for quantum information processing [2–17]. The study of control of these systems is interesting from the perspective of quantum control as the dynamics of coupled electron-nuclear systems has some salient differences compared to coupled nuclear spin systems [18].

The Rabi frequency of the electron (at typical microwave power in pulsed EPR experiments) is of orders of magnitude larger than the Rabi frequency of the nucleus (at typical rf power). The duration of $\frac{\pi}{2}$ pulses on the electron and nucleus are in the nanosecond and microsecond regimes, respectively, in EPR experiments. Local rotations of electrons, therefore, take much less time than the nucleus. The energy eigenstates of the nucleus (at field strengths where hyperfine interactions and the Larmor frequency of the spins are comparable) depend on the state of the electron and are not aligned with the static B_0 field. This results in the well-studied phenomenon of electron spin echo envelop modulation (ESEEM) [1]. This opens the possibility of controlling the nucleus by only manipulating the electron spin [2]. Here we show that universal control of nuclear spin states can be achieved by simply switching the state of the electron between its two eigenstates (by a series of π pulses and delays). The quantization axis and the precession frequency (around this axis) of the nucleus are switched every time the state of electron spin is flipped, making the nucleus nutate around the new quantization axis. We will show that by performing a sequence of flips of the electron (each followed by a suitable delay), we can perform any desired rotation of the nuclear spin states. This rotation can also be conditioned on the state of the electron spin. This mode of control of nuclear spin states obtained by switching between two rotation axes is an excellent example of so-called switched control systems in control theory [19]. Controlling nuclear spin by switching the quantization axis is preferable than rotating nuclear spin with rf fields as hyperfine couplings are orders of magnitude larger than the Rabi frequency of nuclear spin obtainable with typical radio frequency power. Therefore much shorter experiments can be designed, which can significantly reduce relaxation losses, mainly arising from short transverse relaxation times of electron (see example 1, Sec. IV). Furthermore, since the only manipulation required involves flipping the state of the electron spin, we show that it is easy to design these experiments so that they are robust to the Larmor frequency dispersion of the electrons. It is expected that this switched-mode control of nuclear spins will find applications in quantum information processing and pulsed EPR, including pulsed dynamic nuclear polarization (DNP) experiments [1,20].

The paper is organized as follows. In Sec. II, we describe the Hamiltonian that governs the evolution of coupled electron-nuclear spin-$\frac{1}{2}$ system. We show how the nuclear spin is quantized along two different axis depending upon the state of the electron spin. In Sec. III, we show how this feature is exploited to transform between eigenstates of electron-nuclear spin system by simply performing a sequence of π pulses on the electron (each followed by a suitable delay). The number of π pulses required to perform rotations of the nuclear spin is related to the angle between the two quantization axes of the nuclear spin. In Sec. IV, these methods are generalized to perform arbitrary rotations of nuclear spin conditioned on the state of electron spin. We present an algorithm for computing the timing of a sequence of π pulses on the electron spin required to synthesize any desired rotation of the nuclear spin conditioned on the state of electron spin. In Sec. V, we generalize these methods to produce an arbitrary unitary transformation of the electron-nuclear spin system by again simply flipping the electron spin. We also discuss how these methods generalize to a single electron spin coupled to many nuclei.

*navin@hrl.harvard.edu

II. PHYSICAL MODEL

We consider as our model a spin system consisting of one electron spin $S=\frac{1}{2}$ and one nuclear spin $I=\frac{1}{2}$ (see, e.g., Sec. 3.5 of [1]) in a static magnetic field B_0 along the z direction. We will later also discuss the case of one electron coupled to many nuclear spins. Given the Pauli matrices $\sigma_x := \left(\begin{smallmatrix}0&1\\1&0\end{smallmatrix}\right)$, $\sigma_y := i\left(\begin{smallmatrix}0&-1\\1&0\end{smallmatrix}\right)$, and $\sigma_z := \left(\begin{smallmatrix}1&0\\0&-1\end{smallmatrix}\right)$ and the identity matrix $\sigma_0 := \left(\begin{smallmatrix}1&0\\0&1\end{smallmatrix}\right)$, the operators S_j and I_k $(j,k \in \{x,y,z\})$ are defined by $S_j = (\sigma_j \otimes \sigma_0)/2$ and $I_k = (\sigma_0 \otimes \sigma_k)/2$ (see [18]). Let $\mathbf{x},\mathbf{y},\mathbf{z}$ denote standard unit vectors in the x,y,z directions.

The Hamiltonian H_0 of the electron-nuclear spin system (in units so that $\hbar=1$) in the laboratory frame may be written as

$$H_0 = \omega_s S_z + \omega_I I_z + \mathbf{S}\cdot\mathcal{A}\cdot\mathbf{I},$$

where ω_s represents the Larmor precession frequency of the electron spin, ω_I represents Larmor precession frequency of the nuclear spin, and $\mathcal{A}$ is the electron-nuclear hyperfine coupling tensor. Here $\omega_s = -\gamma_e B_0$ and $\omega_I = -\gamma_n B_0$. Here γ_e is the gyromagnetic ratio of the electron (negative) and γ_n is the gyromagnetic ratio of the nucleus (we take it to be positive, as for a proton). At a magnetic field strength of $B_0 \approx 0.5$ T, $\frac{|\omega_I|}{2\pi} = 21.42$ MHz and $\frac{|\omega_S|}{2\pi} = 14.28$ GHz. The hyperfine coupling tensor $\mathcal{A}$ includes the electron spin-nuclear spin Fermi contact interaction (isotropic part of $\mathcal{A}$) and the electron spin-nuclear spin dipolar interaction (anisotropic part of $\mathcal{A}$). As our model $1e$-$1n$ physical system, we consider a single crystal of x-ray-irradiated malonic acid [21]. In this system, the principal values of the hyperfine coupling tensor $\mathcal{A}$ have been measured to be $(\lambda_1,\lambda_2,\lambda_3) = 2\pi(-60,-90,-30)$ MHz [21].

The static field B_0 sets the quantization axis of electron spin, and the coupling Hamiltonian $H_c = \mathbf{S}\cdot\mathcal{A}\cdot\mathbf{I}$ averages to

$$H_c = \mathcal{A}_{zz} S_z I_z + \mathcal{A}_{zx} S_z I_x + \mathcal{A}_{zy} S_z I_y,$$

where the parameters $(\mathcal{A}_{zz},\mathcal{A}_{zx},\mathcal{A}_{zy})$ depend on the principal values $(\lambda_1,\lambda_2,\lambda_3)$ of the coupling tensor $\mathcal{A}$ and the orientation of the crystal with respect to the magnetic field $B_0\mathbf{z}$. The transverse plane axis for the nuclear spin subspace can be so chosen so that the last two terms are combined to form

$$H_c = A S_z I_z + B S_z I_x,$$

where $A = \mathcal{A}_{zz}$ and $B = \sqrt{\mathcal{A}_{zx}^2 + \mathcal{A}_{zy}^2}$. The full Hamiltonian of the system then takes the form

$$H_0 = \omega_s S_z + \omega_I I_z + A S_z I_z + B S_z I_x.$$

In the rotating frame (rotating with the electron at frequency ω_s), the Hamiltonian of the electron-nuclear spin system takes the form

$$H_1 = \Omega_S S_z + \omega_I I_z + A S_z I_z + B S_z I_x,$$

where Ω_S is the resonance offset for the electron. We assume for now that the precession frequency of the electron is well defined and $\Omega_S = 0$ (the case when $\Omega_S \neq 0$ will be discussed subsequently). Let α and β denote the state of the electron spin oriented along and opposite to the direction of the static magnetic field B_0, respectively. For an electron, the α configuration has higher energy than the β configuration.

When the electron is in the α state, the nucleus sees a net field

$$\mathbf{B}_\alpha = \left(B_0 - \frac{A}{2\gamma_n}\right)\mathbf{z} - \frac{B}{2\gamma_n}\mathbf{x}.$$

When the electron is in the β state, the nucleus sees a net field

$$\mathbf{B}_\beta = \left(B_0 + \frac{A}{2\gamma_n}\right)\mathbf{z} + \frac{B}{2\gamma_n}\mathbf{x}.$$

The nuclear precession frequency in the two states is given by

$$\omega_\alpha = \sqrt{\left(\frac{A}{2} + \omega_I\right)^2 + \frac{B^2}{4}}, \quad \omega_\beta = \sqrt{\left(\frac{A}{2} - \omega_I\right)^2 + \frac{B^2}{4}}, \tag{1}$$

where ω_I is negative. We define the operators $S^\alpha = \left(\frac{1}{2} + S_z\right)$ and $S^\beta = \left(\frac{1}{2} - S_z\right)$. Then the Hamiltonian H_1 can be written as

$$H_1 = \omega_I (S_z^\alpha + S_z^\beta) I_z + \frac{(S_z^\alpha - S_z^\beta)}{2}(A I_z + B I_x),$$

which when rewritten looks like

$$H_1 = S_z^\alpha\left(\omega_I I_z + \frac{(A I_z + B I_x)}{2}\right) + S_z^\beta\left(\omega_I I_z - \frac{(A I_z + B I_x)}{2}\right),$$

which is rewritten as

$$H_1 = S^\alpha D_\alpha + S^\beta D_\beta,$$

$$D_{\alpha,\beta} = -\gamma_n \mathbf{I}\cdot\mathbf{B}_{\alpha,\beta} \tag{2}$$

Let $\mathbf{d}_\alpha$ and $\mathbf{d}_\beta$ denote unit vectors along the field directions $\mathbf{B}_\alpha$ and $\mathbf{B}_\beta$. The states $|\alpha+\rangle$ and $|\alpha-\rangle$ represent the state of the spin system when nuclear spin is oriented along or against $\mathbf{d}_\alpha$, respectively, and the electron is in the α state. These states constitute the α manifold. Similarly, the states $|\beta+\rangle$ and $|\beta-\rangle$ represent the state of the spin system when nuclear spin is oriented along or against the field $\mathbf{d}_\beta$, respectively, and the electron is in the β state. These states constitute the β manifold. Figure 1 depicts the field $\mathbf{B}_\alpha$ and $\mathbf{B}_\beta$ and the energy eigenstates of the electron-nuclear spin system when $|\omega_I| > \frac{A}{2}$.

III. CONTROLLING EIGENSTATES OF THE ELECTRON-NUCLEAR SPIN SYSTEM

We now show that starting in an eigenstate of the spin system, switching between the α and β states of the electron by π pulses, we can synthesize any desired rotation of the nuclear spin. Furthermore, since $\omega_\alpha \neq \omega_\beta$, we will show in Sec. (4) that these rotations can be conditioned on the electronic spin state.

To fix ideas, consider the state transformation

$$|\beta+\rangle \rightarrow |\beta-\rangle.$$

When the electron is flipped from the β to α state, the effective field felt by the nucleus switches from direction $\mathbf{d}_\beta$ to $\mathbf{d}_\alpha$

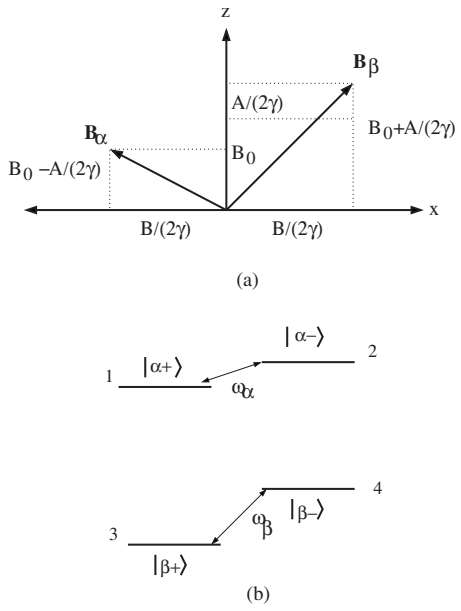

FIG. 1. (a) depicts the field vectors $\mathbf{B}_\alpha$ and $\mathbf{B}_\beta$ when $|\omega_I| > \frac{A}{2}$ and $A > 0$. (b) depicts the corresponding energy-level diagram for the electron-nuclear spin system. Note $\omega_\beta > \omega_\alpha$.

and the nuclear spin begins to precess around this new axis. Following this precession for time τ_1, we flip the electron back, causing the precession axis to return to $\mathbf{d}_\beta$ and then let the precession happen for time τ_2 and so on. Since $\mathbf{d}_\alpha$ and $\mathbf{d}_\beta$ are two independent axes of rotation, switching between them followed by precession can generate any three-dimensional rotation of the nuclear orientation. Figure 2(a) shows the trajectories of nuclear spin on the Bloch sphere as it precesses around the $\mathbf{d}_\alpha$ and $\mathbf{d}_\beta$ directions. These trajectory plots can be used to construct the sequence of switchings between the axis (and delays between switchings) $\mathbf{d}_\alpha$ and $\mathbf{d}_\beta$

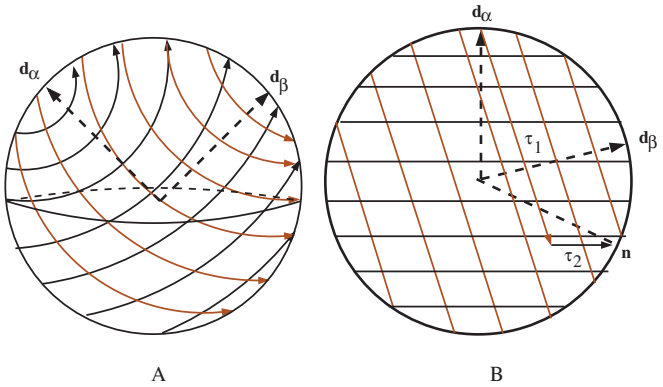

FIG. 2. (Color) (A) shows the trajectories of nuclear spin on the Bloch sphere, as it precesses around the $\mathbf{d}_\alpha$ and $\mathbf{d}_\beta$ directions. This trajectory plot aids in visual construction of rotation between points on the sphere by alternation between rotations around $\mathbf{d}_\alpha$ and $\mathbf{d}_\beta$. (B) depicts one such construction (projected on the plane of axes $\mathbf{d}_\alpha$ and $\mathbf{d}_\beta$) that rotates unit vector $\mathbf{d}_\alpha$ to the unit direction $\mathbf{n}$. The initial rotation is around axis $\mathbf{d}_\beta$ for time τ_1, followed by rotation around $\mathbf{d}_\alpha$ for time τ_2. The times τ_1, τ_2 can be explicitly computed from the figure based on the algorithm described above.

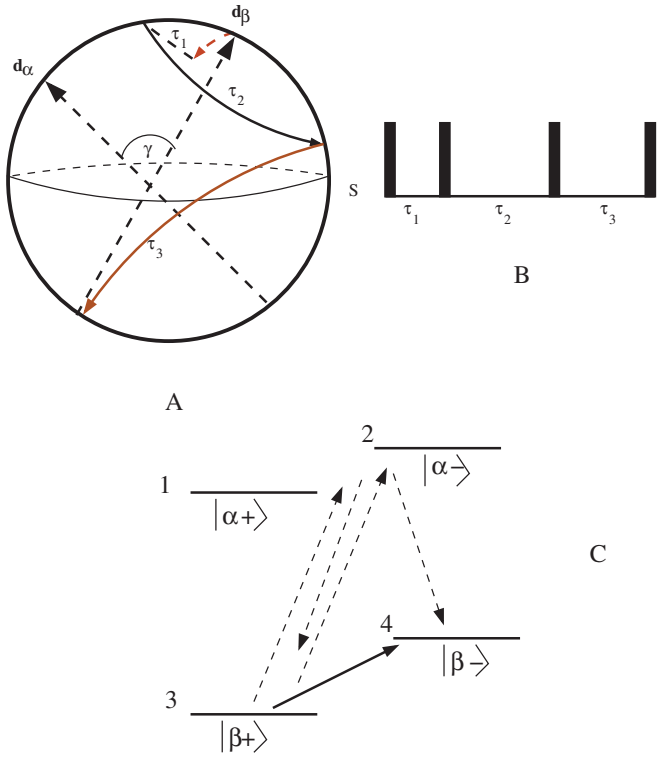

FIG. 3. (Color) (A) depicts the trajectory executed by nuclear spin magnetization, initially oriented along the direction $\mathbf{d}_\beta$, when the pulse sequence in (B) is implemented. The transformation is the inversion of the nuclear spin resulting in the transformation $|\beta+\rangle \rightarrow |\beta-\rangle$. (C) shows that the desired rotation (shown with solid arrow) $|\beta+\rangle \rightarrow |\beta-\rangle$ is implemented by switching the electron between α and β manifolds.

to produce the desired rotation of nuclear the spin state. A simple algorithm for computing such switchings is depicted through Fig. 2(b) [which is a projection of Fig. 2(a) on the plane of axes $\mathbf{d}_\alpha$ and $\mathbf{d}_\beta$] where the initial vector $\mathbf{d}_\alpha$ is transformed to the target vector $\mathbf{n}$. The initial and target vectors can be indexed by the pair (r,s), representing their latitude [black lines indexed from (0, 2), based on the distance from the north pole] and tilted longitudes [brown lines indexed (0, 2) based on the perpendicular distance from the tip of vector $\mathbf{d}_\beta$], respectively. Rotations around $\mathbf{d}_\beta$ and $\mathbf{d}_\alpha$ change r and s, respectively. Rotation is carried out around each axis until the changing coordinate either reaches the respective coordinate for the target vector or reaches the upper limit of how close it can come to the target coordinate, at which point one switches to rotation around the other axis. The process is continued until we reach the (r,s) coordinate of the target vector. The very last evolution time may then be extended to reach the out-of plane coordinate of vector $\mathbf{n}$.

Figure 3 shows the transformation $|\beta+\rangle \rightarrow |\beta-\rangle$, with a three-period pulse sequence. This is a special case of the transformation shown in Fig. 2(b), where the starting vector is oriented along $\mathbf{d}_\beta$ and the final vector $\mathbf{n} = -\mathbf{d}_\beta$. The delays τ_1, τ_2, and τ_3 are chosen so that the nuclear spin magnetization executes the trajectory shown in Fig. 3(a). The last π pulse in the figure returns the electron to state β. The times τ_1, τ_2, and τ_3 can be computed from this figure.

Similar arguments can be used to transform any energy eigenstate into another by simply flipping the electron spins followed by appropriate delays. This then naturally leads us to the question of the number of times the state of the electron needs to be switched to produce any desired rotation of the nuclear spins in a given eigenstate in either α or β manifold. The problem of finding the minimum number of switchings for producing arbitrary rotations by switching between two axes of rotation has been studied before. We recapitulate the main results and motivate further extensions.

Remark 1: uniform generation. Let γ denote the angle between two rotation axes $\mathbf{d}_\alpha$ and $\mathbf{d}_\beta$ as shown in Fig. 3. Then it is a known result [22] that any three-dimensional rotation in group SO(3) [similar result holds for group SU(2)] can be constructed by not more than $k+2$ rotations (performed around $\mathbf{d}_\alpha$ or $\mathbf{d}_\beta$), where

$$\frac{\pi}{k+1} \leqslant \gamma < \frac{\pi}{k}.$$

Therefore, starting in either the α or β manifold, any rotation of nuclear spin can be obtained by a pulse sequence as shown in Fig. 3(b) with no more that $k+2$ evolution periods τ_i. Furthermore, there exist algorithms to find the sequence with a minimum number of switches [23] to generate any arbitrary rotation using only rotations around $\mathbf{d}_\alpha$ and $\mathbf{d}_\beta$. Here, we present a strategy for obtaining such a sequence (which need not be minimal in terms of the number of switches) which is easy to construct geometrically.

Let $\tau_1 - \tau_k$ (k even) be the times for alternate rotations (starting with $\mathbf{d}_\beta$) around $\mathbf{d}_\beta$ and $\mathbf{d}_\alpha$, with angular frequency ω_β and ω_α, so chosen that the resulting rotation takes the initial vector $\mathbf{d}_\alpha$ to unit direction $\mathbf{n}$ as described in Fig. 2(b). Let $U(\alpha,\tau)=\exp(-i\omega_\alpha \tau \mathbf{d}_\alpha \cdot \boldsymbol{\sigma})$ and $U(\beta,\tau)=\exp(-i\omega_\beta \tau \mathbf{d}_\beta \cdot \boldsymbol{\sigma})$ be rotations in SU(2) around axes $\mathbf{d}_\alpha$ and $\mathbf{d}_\beta$. A rotation by the angle θ around a unit vector $\mathbf{n}=n_x\mathbf{x}+n_y\mathbf{y}+n_z\mathbf{z}$ takes the form

$$\exp(-i\theta \mathbf{n}\cdot\boldsymbol{\sigma}) = \cos\frac{\theta}{2}\mathbf{1} - i2\sin\frac{\theta}{2}\mathbf{n}\cdot\boldsymbol{\sigma}, \tag{3}$$

where $\mathbf{n}\cdot\boldsymbol{\sigma}=n_x\sigma_x+n_y\sigma_y+n_z\sigma_z$. Then, a sequence of rotations

$$\underbrace{U(\alpha,\tau_k)\cdots U(\beta,\tau_1)}_{U_1} U(\alpha,\tau) \underbrace{U(\beta,-\tau_1)\cdots U(\alpha,-\tau_k)}_{U_1^{-1}} \tag{4}$$

will generate a rotation around the unit vector $\mathbf{n}$ with an angle $\theta=\tau\omega_\alpha$. Let

$$t_\alpha = \frac{2\pi}{\omega_\alpha}, \quad t_\beta = \frac{2\pi}{\omega_\beta}. \tag{5}$$

The rotations $U(\beta,-\tau)$ and $U(\alpha,-\tau)$ are simply obtained by observing that

$$U(\beta,t_\beta-\tau) = -U(\beta,-\tau), \quad U(\alpha,t_\alpha-\tau) = -U(\alpha,-\tau). \tag{6}$$

Since k is even, the negative signs in (4) cancel out (if k is odd, it just produces a global phase).

In the following section, we generalize these results and show how to design a sequence of π pulses of electron spin that produces a desired rotation of the nuclear spin conditioned on the state of the electron spin.

IV. SYNTHESIS OF CONTROLLED OPERATIONS ON NUCLEAR SPINS

A α manifold-selective controlled operation on the nuclear spin transforms $|\alpha+\rangle \to U|\alpha+\rangle$ and $|\alpha-\rangle \to U|\alpha-\rangle$, where $U \in \mathrm{SU}(2)$ is a unitary transformation that mixes states $|\alpha+\rangle$ and $|\alpha-\rangle$. The β manifold is left unperturbed—i.e., $|\beta+\rangle \to |\beta+\rangle$ and $|\beta-\rangle \to |\beta-\rangle$. We show that such controlled operations can again be performed by toggling the state of the electron spin with π pulses, followed by suitable delays. This is best seen by observing that by flipping the state of the electron spin, we can switch between the Hamiltonians

$$H_1 = \omega_I I_z + S_z(AI_z + BI_x) \tag{7}$$

and

$$H_2 = \omega_I I_z - S_z(AI_z + BI_x), \tag{8}$$

where evolution under H_2 is obtained as

$$\exp(-iH_2\tau_2) = \exp(-i\pi S_x)\exp(-iH_1\tau_2)\exp(-i\pi S_x). \tag{9}$$

Therefore, the pulse sequence τ_1-π-τ_2-π (where the π pulse is on the electron) evolves H_1 for time τ_1, followed by H_2 for time τ_2. A straightforward calculation shows that when $\omega_\alpha \neq \omega_\beta$ [in Eq. (1)], the repeated commutators of $-iH_1$ and $-iH_2$ generate a six-dimensional algebra, spanned by generators $\mathfrak{k}=-i\{I_x,I_y,I_z,S_zI_z,S_zI_x,S_zI_y\}$. Then a standard result of controllability [24] states that any unitary transformation generated by these generators can be produced by simply switching between $-iH_1$ and $-iH_2$; i.e., any rotation of the kind

$$\exp[-i(aS_zI_p + bI_q)], \tag{10}$$

where I_p and I_q are nuclear spin operators, can be synthesized by switching between $-iH_1$ and $-iH_2$. Specifically, we can perform a rotation $\exp(-iS^\alpha I_\gamma)$, which only rotates nuclear spins in the electron's α manifold [$S^\alpha=(\frac{1}{2}+S_z)$, $S^\beta=(\frac{1}{2}-S_z)$].

We can write the Hamiltonians H_1 and H_2 in block-diagonal form [see Eq. (2)] as

$$H_1 = \begin{pmatrix} D_\alpha & 0 \\ 0 & D_\beta \end{pmatrix}, \quad H_2 = \begin{pmatrix} D_\beta & 0 \\ 0 & D_\alpha \end{pmatrix},$$

where $D_{\alpha,\beta}$ denotes the generator of rotation around the axis $\mathbf{d}_{\alpha,\beta}$ with angular, frequency $\omega_{\alpha,\beta}$. The algebra $\mathfrak{k}$ is simply all block-diagonal 6×6 skew Hermitian matrices—i.e., matrices of the form

$$\begin{pmatrix} A_1 & 0 \\ 0 & A_2 \end{pmatrix},$$

where $A_1=-A_1^\dagger$ and $A_2=-A_2^\dagger$. Note, in the special case when $A=0$ in Eqs. (1), then $\omega_\alpha=\omega_\beta$ in Eqs. (1). In this special case,

the algebra generated by H_1 and H_2 is only a three-dimensional algebra and we cannot produce arbitrary controlled operations on the nuclei. This case, however, is of only theoretical interest and will not be considered any further.

A π pulse on the electron will switch H_1 to H_2 and vice-versa. A sequence of delays and flips, τ_1-π-τ_2-$\cdots$-τ_k-π, where k is, say, even, will execute the following rotations on the nuclear spin in α and β manifolds, respectively:

$$U_\alpha = U(\beta,\tau_k)\cdots U(\alpha,\tau_1), \quad U_\beta = U(\alpha,\tau_k)\cdots U(\beta,\tau_1).$$

Here $U(\alpha,\tau)=\exp(-iD_\alpha\tau)$ and $U(\beta,\tau)=\exp(-iD_\beta\tau)$. The goal is to find the sequence of times τ_k, such that $U_\beta=I$ and $U_\alpha=U_f$ is the desired rotation. This constitutes a controlled rotation on nuclear spins, conditioned on the electron state. Similarly, finding a sequence of times τ_k, such that $U_\beta=U_\alpha=U_f$, constitutes a uniform rotation of the nuclear spin state. In general, we want to find a sequence that performs manifold-selective operations; i.e., U_α and U_β are as desired. It is also a known result [22] that there exists a finite number of switchings, N, such that arbitrary U_α and U_β can be constructed by no more than N number of switchings. Finding methods to generate these in a minimum number of switchings is an interesting problem in the present context. We present a constructive search strategy for achieving this (our methods need not be minimal in terms of number of switching).

Let us perform a series of rotations on the β manifold (with k even) given by

$$U_\beta = \underbrace{U(\beta,-\tau_1)\cdots U(\alpha,-\tau_k)}_{U_1^{-1}}\underbrace{U(\alpha,\tau_k)\cdots U(\beta,\tau_1)}_{U_1},$$

where U_β is implemented as

$$U_\beta = U(\beta,t_\beta-\tau_1)\cdots U(\alpha,t_\alpha-\tau_k)U(\alpha,\tau_k)\cdots U(\beta,\tau_1).$$

By definition, $U_\beta=\mathbf{1}$. We now have the independence in selecting $\tau_1-\tau_k$, in such a way that the corresponding rotation of the α manifold is given by

$$\underbrace{U(\alpha,t_\beta-\tau_1)\cdots U(\beta,t_\alpha-\tau_k)}\underbrace{U(\beta,\tau_k)\cdots U(\alpha,\tau_1)} = U_F. \tag{11}$$

We rewrite this relation as

$$1 = \underbrace{U(\beta,\tau_k-t_\alpha)\cdots U(\alpha,\tau_1-t_\beta)}U_F\underbrace{U(\alpha,-\tau_1)\cdots U(\beta,-\tau_k)}. \tag{12}$$

Equation (12) can then be written as

$$1 = \underbrace{BU(\beta,\tau_k)\cdots\underbrace{AU(\alpha,\tau_1)U_FU(\alpha,-\tau_1)}_{U_F^1}\cdots U(\beta,-\tau_k)}_{U_F^k}, \tag{13}$$

where $A=U(\alpha,-t_\beta)$ and $B=U(\beta,-t_\alpha)$.

Equation (13) can be used to determine $\tau_1-\tau_k$. In Eq. (13), the times $\tau_1-\tau_k$, are chosen to increase the trace of U_F^k to 2 [the only matrix in SU(2) with trace 2 is $\mathbf{1}$]. These can be obtained iteratively in a closed form by the following optimization procedure. Suppose $\tau_2-\tau_k$ is fixed. Now, Eq. (13) can be written as

$$\mathrm{Tr}(U_F^k) = \mathrm{Tr}[C_1U(\alpha,\tau_1)U_FU(\alpha,-\tau_1)], \tag{14}$$

where

$$C_1 = U(\beta,-\tau_2)\cdots U(\beta,-\tau_k)BU(\beta,\tau_k)AU(\alpha,\tau_{k-1})\cdots A.$$

The time τ_1 is chosen to maximize $\mathrm{Tr}(U_F^k)$. The quantity to optimize then takes the form

$$\mathrm{Tr}[C_1U(\alpha,\tau_1)U_FU(\alpha,-\tau_1)] = 2\left\{\cos\frac{\theta}{2}\cos\frac{\theta_c}{2} - \sin\frac{\theta}{2}\sin\frac{\theta_c}{2}\mathbf{n}_c\cdot\mathbf{n}(\tau_1)\right\}, \tag{15}$$

where $U_F=\exp(-i\theta\mathbf{n}\cdot\boldsymbol{\sigma})$ and $C_1=\exp(-i\theta_c\mathbf{n}_c\cdot\boldsymbol{\sigma})$. Let

$$\mathbf{n}_\parallel = (\mathbf{n}\cdot\mathbf{d}_\alpha)\mathbf{d}_\alpha, \quad \mathbf{n}_\perp = \mathbf{n}-\mathbf{n}_\parallel. \tag{16}$$

Similarly define

$$(\mathbf{n}_c)_\parallel = (\mathbf{n}_c\cdot\mathbf{d}_\alpha)\mathbf{d}_\alpha, \quad (\mathbf{n}_c)_\perp = \mathbf{n}_c-(\mathbf{n}_c)_\parallel. \tag{17}$$

In expression (15), τ_1 generates a rotation around the axis $\mathbf{d}_\alpha$ and only rotates $\mathbf{n}_\perp$, the part of $\mathbf{n}$, that is perpendicular to $\mathbf{d}_\alpha$. We can rewrite Eq. (15) as

$$\mathrm{Tr}[C_1U(\alpha,\tau_1)U_FU(\alpha,-\tau_1)] = 2\left\{\cos\frac{\theta}{2}\cos\frac{\theta_c}{2} - \sin\frac{\theta}{2}\sin\frac{\theta_c}{2}[(\mathbf{n}_c)_\perp\cdot\mathbf{n}_\perp(\tau_1) + \mathbf{n}_\parallel\cdot(\mathbf{n}_c)_\parallel]\right\}. \tag{18}$$

See Fig. 4. The expression in Eq. (18) is maximized when $\mathbf{n}_\perp(\tau_1)$ is aligned or anti aligned (depending on the sign of $\sin\frac{\theta}{2}\sin\frac{\theta_c}{2}$) with $(\mathbf{n}_c)_\perp$. We can write an explicit expression for τ_1. Let $\mathbf{a}$ be a unit vector in the direction of $\sin\frac{\theta}{2}\mathbf{n}_\perp$ and $\mathbf{b}$ be a unit vector in the direction of $\sin\frac{\theta_c}{2}(\mathbf{n}_c)_\perp$; then, $\sin(\omega_\alpha\tau_1)=(\mathbf{b}\times\mathbf{a})\cdot\mathbf{d}_\alpha$. Having determined the optimal value τ_1, we can now proceed to maximize τ_2 which is now an optimization of a function like $\mathrm{Tr}[C_2U(\beta,\tau_2)U_F^1U(\beta,-\tau_2)]$ and so on. Having found a set of values $\tau_1-\tau_k$, this way, we iterate again. Note that $\mathrm{Tr}(U_F^k)$ is bounded above by 2. By construction, each iteration increases the value of $\mathrm{Tr}(U_F^k)$ and therefore this monotonically nondecreasing process has a limit, proving that the algorithm converges. If this limit value

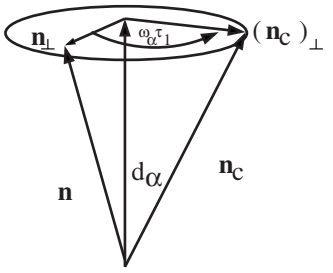

FIG. 4. Depiction of the geometry of vectors $\mathbf{n}$, $(\mathbf{n}_c)$, $\mathbf{n}_\perp$, $(\mathbf{n}_c)_\perp$, and $\mathbf{d}_\alpha$.

is not 2, we can increase k and repeat the iteration. The resulting set of evolution times $\tau_1 - \tau_k$ synthesizes a selective rotation of the α manifold as in Eq. (11). Similarly we can synthesize a selective rotation of the β manifold and therefore any rotation of the kind given in Eq. (10). Alternatively, we can synthesize a desired unitary transformation U_β on the β manifold as described in Eq. (4), which results in some rotation U'_α of the α manifold (which is easily computed). Now performing an α-manifold-selective rotation of $U_\alpha (U'_\alpha)^{-1}$ will result in the desired rotations of the two manifolds.

Example 1. Using the above-described method, we explicitly compute the pulse sequence for implementing a controlled rotation $\exp(-i\pi S^\alpha I_y)$, which inverts the nuclear spins in the α manifold and leaves the β manifold unaffected. As our model $1e$-$1n$ physical system, we consider a single crystal of x-ray-irradiated malonic acid [2,21]. The RCHR radical (R=-COOH) in malonic acid represents a prototypical $>\dot{C}H$ fragment, where the unpaired electron in a $2p$ π orbital on carbon interacts with a directly bonded proton. In this system, the principal values of the hyperfine coupling tensor $\mathcal{A}$ have been measured to be $(\lambda_1,\lambda_2,\lambda_3)=2\pi(-90,-60,-30)$ MHz.[21] The coupling tensor is composed of an isotropic part with the measured value of -60 MHz and an anisotropic part with principal values $(\lambda_1^a,\lambda_2^a,\lambda_3^a)=2\pi(-30,0,30)$ MHz. Let $\mathbf{e}_1,\mathbf{e}_2,\mathbf{e}_3$ represent principal vectors corresponding to $(\lambda_1^a,\lambda_2^a,\lambda_3^a)$ respectively. If we orient the crystal, such that the magnetic field $B_0\mathbf{z}$ lies in the $\mathbf{e}_2$-$\mathbf{e}_3$ plane, making an angle of $\frac{\pi}{4}$ with both the vectors, then the hyperfine coupling tensor $\mathcal{A}$, with the y axis taken along $\mathbf{e}_1$, takes the form

$$\frac{\mathcal{A}}{2\pi}=\left(\underbrace{-60\ 1}_{\text{isotropic}}+\underbrace{\begin{pmatrix}-30 & 0 & 15\\ 0 & 0 & 0\\ 15 & 0 & 15\end{pmatrix}}_{\text{anisotropic}}\right)=\begin{pmatrix}-90 & 0 & 15\\ 0 & -60 & 0\\ \underbrace{15}_{\mathcal{A}_{zx}} & 0 & \underbrace{-45}_{\mathcal{A}_{zz}}\end{pmatrix}\text{MHz}.$$

Therefore $A/(2\pi)=-45$ MHz and $B/(2\pi)=15$ MHz and at a magnetic field strength of $0.5T$, $\frac{|\omega_I|}{2\pi}=21.42$ MHz and $\frac{|\omega_S|}{2\pi}=14.28$ GHz. This gives $\frac{\omega_I}{A}=-0.4762$ and $\frac{B}{A}=-1/3$. The pulse sequence $\underbrace{\tau_1-\pi\ldots\tau_7}_{P}$, where the switching times, in units of $1/A$, are $\tau_1=1.3748$, $\tau_2=6.2108$, $\tau_3=6.1908$, $\tau_4=25.52$, $\tau_5=30.21$ and $\tau_6=19.31$, $\tau_7=35.02$, implements the desired controlled rotation. The total time, in units of $1/A$, is 123.84 and corresponds to 0.438 μs. Assuming a moderately high rf power with Rabi frequency of 100 Mhz for the nuclear spin, the duration of a π pulse will take 5 μs. Therefore, the proposed methodology of the paper is more than an order of magnitude faster than using rf rotation of the nucleus.

Also note that using the above sequence as a building block, the pulse sequence P-π-P-π implements the rotation

$$\exp[-i\pi(S^\alpha+S^\beta)I_y]=\exp(-i\pi I_y).$$

Similarly let Q denote the switching sequence that implements $\exp(-i\pi I_x)$. Then the pulse sequence P-Q-π-P-π-Q will implement the rotation

$$\exp[-i\pi(S^\alpha-S^\beta)I_y]=\exp(-i\pi 2I_zS_y).$$

V. UNITARY TRANSFORMATIONS OF COUPLED SPIN SYSTEMS

We now show how any arbitrary unitary transformation of the electron-nuclear spin system can be synthesized by a sequence of π pulses of the electron in combination with single spin rotations of the electron. Any unitary transformation U_F of the electron-nuclear spin system is given by [25]

$$U_F=U_IU_S\exp[-i(aS_xI_x+bS_yI_y+cS_zI_z)]V_IV_S,$$

where U_I,V_I are single-spin operations on the nucleus and U_S,V_S are single-spin operations on the electron. The operators I_xS_x, I_yS_y, and I_zS_z all commute. As described in Eq. (10), we have shown that all rotations of the kind $\exp(-i\theta_1S_zI_a)$ and $\exp(-i\theta_2I_b)$ can be synthesized by simply toggling electron spins (here I_a and I_b are arbitrary nuclear spin operators). These rotations, along with single-spin rotations $\exp(-i\theta_3S_\gamma)$, of the electron can be used to perform arbitrary unitary rotation on the electron-nuclear spin system. The bilinear rotations $\exp(-i\theta S_xI_x)$ can be synthesized as

$$\exp(-i\theta S_xI_x)=\exp\left(-i\frac{\pi}{2}S_y\right)\exp(-i\theta S_zI_x)\exp\left(i\frac{\pi}{2}S_y\right),$$

$$\exp(-i\theta S_yI_y)=\exp\left(i\frac{\pi}{2}S_x\right)\exp(-i\theta S_zI_y)\exp\left(-i\frac{\pi}{2}S_x\right),$$

where $\exp(-i\theta S_zI_x)$ and $\exp(-i\theta S_zI_y)$ can be generated by a sequence of π pulses of the electron as described in Sec. (4).

Remark 2: refocusing resonance offsets for electron spins. In the above-described methods, we have assumed that the precession frequency of the electron is precisely defined and there are no resonance offsets. The dispersion in the frequency of the electron can be refocused by the following

technique. For k even, let τ_1-π-τ_2-$\cdots$-τ_k-π be a sequence that implements the propagator $U_f=\exp(-i\frac{b}{2}I_q)$. Then the sequence P-P, where $P=\tau_1$-π-τ_2-$\cdots$-τ_k, will implement the propagator $\exp(-ibI_q)$ and refocus all resonance effects. Observe that the free evolution for time τ corresponds to the propagator $\exp(-iH_1\tau)\exp(-i\Omega S_z\tau)$. Observe that there are an odd number of π pulses between the τ_1 evolution periods in the two pulse sequence blocks denoted by P. The evolution $\exp(-i\Omega S_z\tau_1)$ in the two blocks will therefore cancel. A similar argument applies for other free evolution periods. The pulse sequence P implements the propagator $\exp(-i\frac{b}{2}I_q)$, and therefore P-P implements the propagator $\exp(-ibI_q)$.

We now consider the problem of synthesizing a general rotation of the kind $\exp[-i(aS_zI_p)]$, in the presence of resonance offsets. Let I_q be orthogonal to I_p. Let us consider a switching sequence that implements $\exp(-i\pi I_q)$ and compensates for offset effects. We have just described how to construct such a sequence. Consider a switching sequence (assuming no resonance offset) $Q=\tau_1$-π-τ_2-$\cdots$-τ_k such that k is even and Q-π implements $\exp(-i\frac{a}{2}S_zI_p)$. Then the sequence Q-R-Q-R will implement the desired propagator $\exp(-iaS_zI_p)$ and compensate for offset effects on the electron. This is best seen by writing the propagator for Q-R-Q-R. Note that in the presence of resonance offsets Q-π prepares a propagator $U=\exp[-i(\frac{a}{2}S_zI_p+\delta\Omega S_z)]$ for some δ. Then Q-R-Q-R prepares the propagator

$$U\exp[-i\pi(S_x+I_q)]U\exp[-i\pi(S_x+I_q)],$$

which is same as $\exp(-iaS_zI_p)$.

Remark 3: polarization transfer from the electron to nucleus. The above-described methods can now be used to transfer polarization from electrons to the nucleus. We describe a sequence of unitary transformations for transferring polarization from electron to the nucleus. Such polarization transfer operations underly dynamic nuclear polarization (DNP), a magnetic resonance technique utilized to enhance the polarization of nuclei in samples containing paramagnetic centers to increase sensitivity of the NMR experiments [26,27]. The coherent methods of performing such polarization transfer operation rely on manipulating nuclei using rf pulses. As described before at typical rf powers available in these experiments, such manipulations require a significant amount of time compared with the transverse relaxation times of the electron spin, leading to poor polarization transfer efficiency. Here we describe a method for performing such polarization transfer which exploits the large hyperfine couplings and involves only performing a sequence of π and $\frac{\pi}{2}$ pulses on the electrons. No rf manipulation of nuclei is required. It is expected that these techniques will help in a significant improvement in the polarization transfer efficiency of these experiment.

The desired transformation

$$S_z \rightarrow I_z$$

can be performed as follows:

$$S_z \xrightarrow{\exp\left(-i\frac{\pi}{2}S_y\right)} S_x \xrightarrow{\exp\left(-i\frac{\pi}{2}2S_zI_y\right)} 2S_yI_y \xrightarrow{\exp\left(-i\frac{\pi}{2}S_x\right)} 2S_zI_y \xrightarrow{\exp\left(-i\frac{\pi}{2}2S_zI_x\right)} I_z, \tag{19}$$

where the various unitary transformations can be performed in a way that are robust to resonance offsets as described before. Furthermore, all bilinear Hamiltonians above can be synthesized by simply doing π pulses on the electron as described before.

Remark 4: electron coupled to many nuclei. We now consider the coupling Hamiltonian of a single electron $\frac{1}{2}$, coupled to many spin-$\frac{1}{2}$, nuclei. The Hamiltonian for the spin system takes the form [1]

$$H_0=\Omega_SS_z+\sum_{j=1}^{N}\omega_{jI}I_{jz}+S_z\sum_{j=1}^{N}(A_jI_{jz}+B_jI_{jx}).$$

For now, we neglect the resonance offset Ω_S for the electron. As before, for each electron-nuclear coupling, we can define the unit directions $(d_{j\alpha},d_{j\beta})$ and the precession frequencies $(\omega_{j\alpha},\omega_{j\beta})$. Then a straightforward computation shows that if for all j the precession frequencies $\omega_{j\alpha}\neq\omega_{j\beta}$ and the frequency pairs $(\omega_{j\alpha},\omega_{j\beta})\neq(\omega_{k\alpha},\omega_{k\beta})$ are distinct, then all the commutators generated by $-iH_1$ and $-iH_2$, where

$$H_1=\sum_{j=1}^{N}\omega_{jI}I_{jz}+S_z\sum_{j=1}^{N}(A_jI_{jz}+B_jI_{jx})$$

and

$$H_2=\sum_{j=1}^{N}\omega_{jI}I_{jz}-S_z\sum_{j=1}^{N}(A_jI_{jz}+B_jI_{jx}),$$

span the space $\{I_{jp},S_zI_{jq}\}$. Therefore any rotation of the individual nuclei is achievable by simply switching the electron state by π pulses. These rotations combined with rotations of the electron are sufficient to synthesize any unitary transformation of the coupled electron-nuclear spin system. Let $U_{\alpha j}$ and $U_{\beta j}$ represent the desired unitary transformation of the α and β manifolds of the jth nuclei. Let τ_1-π-$\cdots$-π-τ_k-π (k even) be the pulse sequence that implements such a transformation. Then the switching times can be computed by iterative maximization over τ_1-τ_k of a trace function like

$$\sum_j \mathrm{tr}[U'_{\alpha j}U(\beta_j,\tau_k)\cdots U(\alpha_j,\tau_1)] + \mathrm{tr}[U'_{\beta j}U(\alpha_j,\tau_k)\cdots U(\beta_j,\tau_1)],$$

where $U(\alpha_j,\tau)$ represents rotation of the jth nuclei around the axis α_j, with angular frequency $\omega_{\alpha j}$ for time τ. Gradient algorithms for maximization of such trace functions were presented in [28]

VI. CONCLUSION

In this article, we developed techniques for control of coupled electron-nuclear spin systems. We showed that the spin system at magnetic field strengths where the Larmor frequency of the nucleus is comparable to the hyperfine cou-

pling strength can be controlled by simply performing a sequence of flips (each followed by a suitable delay) of the state of the electron spin. We showed that this mode of switched control allows for universal control of the nuclear spin states. This switched control of nuclear spin states is much faster in settings where the hyperfine coupling is much larger than the Rabi frequency of the nucleus. Combined with single-spin rotations of the electron spin, switched-mode control can be used to synthesize any unitary transformation of the coupled spin system. We presented algorithms for explicitly computing the switching times. Furthermore, we discussed how these methods can be made robust to resonance offsets of the electron spin. A further method development is required to make these methods robust to dispersion in strength of hyperfine couplings. Application of these methods for transferring polarization from electron to nuclear spins was also discussed. The switched control methods presented in this work are expected to find applications in pulsed EPR experiments and quantum information processing systems based on coupled electron-nuclear spin dynamics.

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