Switched Control of Electron Nuclear Spin Systems

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In this article, 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 on nuclear spin states. We show that by performing a sequence of flips (each followed by a suitable delay), we can perform any desired rotation on the nuclear spins, 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 on 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 system consisting of an electron, coupled with one or more nuclear spins. Manipulation of such electron-nuclear spin systems is fundamental in the field of ESR/EPR [1] with application to the study of structure and dynamics of paramagnetic species. Coupled electron-nuclear spin systems have recently been studied from the perspective of quantum information processing [2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16]. Study of control of these systems is interesting from perspective of quantum control as dynamics of coupled electron-nuclear system has some salient differences compared to coupled nuclear spin systems [17].

The Rabi frequency of the electron (at typically available microwave power in pulsed EPR experiments) is of orders of magnitude larger than the Rabi frequency of the nucleus (at typical rf-power). Duration of $\frac{\pi}{2}$ pulses on the electron and nucleus are in ns and $\mu$s regimes respectively in EPR experiments. Local rotations on electrons, therefore take much less time than the nucleus. The energy eigenstates of the nucleus (at field strengths where hyperfine interactions and Larmor frequency of the spins is 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 simply manipulating the electron spin between its two eigenstates (by a series of $\pi$ pulses and delays). The quantization axis and the precession frequency (around this axis) of the nucleus is switched every time the state of electron spin is flipped, making the nucleus nutate around the new quantization axis. We will shown that by performing a sequence of flips on the electron (each followed by a suitable delay), we can perform any desired rotation on the nuclear spin states. This rotation can also be conditioned on the

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state of the electron spin. This mode of control on nuclear spins obtained by switching between two rotation axis is an excellent example of so called switched control systems in control theory \[18\]. Controlling nuclei by switching quantization axis is preferable than rotating nuclei with rf-fields as hyperfine couplings are orders of magnitude larger that Rabi frequency 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. 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 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 \[1\], \[19\].

II. THEORY

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., Sect. 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. The Hamiltonian \( H_0 \) of the electron-nuclear spin system in the laboratory frame may be written as

\[
H_0 = \omega_s S_z + \omega_I I_z + S \cdot A \cdot I,
\]

where \( \omega_s \) represents the Larmor precession frequency of the electron spin, \( \omega_I \) represents Larmor precession frequency of the nuclear spin, and \( A \) is the electron-nuclear hyperfine coupling tensor. Given the Pauli matrices \( \sigma_x := \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \), \( \sigma_y := i \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \), and \( \sigma_z := \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \) and the identity matrix \( \sigma_0 := \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \), 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 \[17\]). The static field \( B_0 \), sets the quantization axis of electron spin and the coupling Hamiltonian \( H_c = S \cdot A \cdot I \), averages to

\[
H_c = AS_z I_z + B_x S_z I_x + B_y S_z I_y,
\]

The transverse plane axis for the nuclear spin subspace can be so chosen that the last two terms are combined to form

\[
H_c = AS_z I_z + BS_z I_x,
\]

where \( B = \sqrt{B_x^2 + B_y^2} \). The full Hamiltonian of the system then takes the form

\[
H_0 = \omega_s S_z + \omega_I I_z + AS_z I_z + BS_z I_x.
\]
Here $\omega_s = -\gamma_e B_0$ and $\omega_I = -\gamma_n B_0$. Here $\gamma_e$ is the gyromagnetic ratio of the electron (negative) and $\gamma_n$ is the gyromagnetic ratio of the nucleus (we take positive, as for a proton).

Let $\alpha$ and $\beta$ 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 $\alpha$ configuration has higher energy than the $\beta$ configuration.

When the electron is in the $\alpha$ state, the nucleus sees a net field

$$B_\alpha = (B_0 - \frac{A}{2\gamma_n})\hat{z} - \frac{B}{2\gamma_n}\hat{x}.$$ 

When the electron is in the $\beta$ state, the nucleus sees a net field

$$B_\beta = (B_0 + \frac{A}{2\gamma_n})\hat{z} + \frac{B}{2\gamma_n}\hat{x}.$$ 

The nuclear precession frequency in the two states is given by

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

where $\omega_I$ is negative. Let $d_\alpha$ and $d_\beta$ denote unit vectors along the field directions $B_\alpha$ and $B_\beta$. The states $|\alpha\alpha\rangle$ and $|\alpha\beta\rangle$ represent the states of nuclei oriented along or against $d_\alpha$ respectively, when the electron is in the $\alpha$ state. These states constitute the $\alpha$ manifold. Similarly, the states $|\beta\alpha\rangle$ and $|\beta\beta\rangle$ represent the states of nuclei oriented along or against the field $d_\beta$ respectively, when the electron is in the $\beta$ state. These states constitute the $\beta$ manifold. Fig. 1 depicts the field $d_\alpha$ and $d_\beta$ and the energy eigenstates states when $|\omega_I| > \frac{4}{\gamma_n}$.

FIG. 1: Fig. A depicts the vectors $d_\alpha$ and $d_\beta$ when $|\omega_I| > \frac{4}{\gamma_n}$. Fig. B depicts the corresponding energy level diagram.

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

$$H_1 = \Omega S_z + \omega_I I_z + A S_z I_z + B S_z I_x$$
where $\Omega_S$ is the resonance offset for the electron. We assume for now that precession frequency of the electron is well defined and $\Omega_S = 0$ (the case when $\Omega_S \neq 0$ will be discussed subsequently). We now show how by switching between the $\alpha$ and $\beta$ states of the electron, by $\pi$ pulses, we can synthesize any desired rotation on the spin states of the nuclei. Furthermore, since $\omega_\alpha \neq \omega_\beta$, we will show these rotations can be made conditioned on the electronic state. To fix ideas, consider the state transformation

$$|\beta\alpha\rangle \rightarrow |\beta\beta\rangle.$$

When the electron is flipped from $\beta$ to $\alpha$ state, the effective field felt by the nucleus switches from direction $d_\beta$ to $d_\alpha$ and the nuclei begin to precess around this new axis. Following this precession for time $\tau_1$, we flip the electron back, causing the precession axis to return to $d_\beta$ and then let the precession happen for time $\tau_2$ and so on. Since $d_\alpha$ and $d_\beta$ are two independent axis of rotations, switching between them followed by precession can generate any three dimension rotation of the nuclear orientation. Fig. 2A shows the trajectories of nuclear spin on the Bloch sphere as it precesses around $d_\alpha$ and $d_\beta$ directions. These trajectory plots can be used to construct the sequence of switchings between the axis (and delays between switchings) $d_\alpha$ and $d_\beta$ to produce the desired rotation of nuclear spin state. Fig. 2B, shows one such graphical construction for finding the switching times $\tau_1$, $\tau_2$ and $\tau_3$, that rotates the unit vector $d_\alpha$ to vector $\hat{n}$, by alternate rotations around $d_\beta$ and $d_\alpha$. 

**FIG. 2**: Fig. 2A shows the various trajectories of nuclear spin on the Bloch sphere as it precesses around $d_\alpha$ and $d_\beta$ directions. This trajectory plot aids in visual construction of rotation between points on the sphere by alternation between rotations around $d_\alpha$ and $d_\beta$. Backtracking these trajectories can help to construct desired rotation of nuclear spin state by switching between field directions $d_\alpha$ and $d_\beta$. Fig. 2B depicts one such construction (projected on the plane of axis $d_\alpha$ and $d_\beta$ ) that rotates unit vector $d_\alpha$ to the unit direction $\hat{n}$. The initial rotation is around axis $d_\beta$ for time $\tau_1$, followed by rotation around $d_\alpha$ for time $\tau_2$ and finally around $d_\beta$ for time $\tau_3$. The times $\tau_1$, $\tau_2$ and $\tau_3$ can be explicitly computed from this figure.
Fig. 3 shows the transformation $|\beta\alpha\rangle \rightarrow |\beta\beta\rangle$, with a three period pulse sequence as shown in the Fig. 3. The delays $\tau_1$, $\tau_2$ and $\tau_3$ are chosen so that the nuclear spin magnetization execute the trajectory shown in Fig. 3A. The last $\pi$ pulse in the figure returns the electron to state $\beta$. The times $\tau_1$, $\tau_2$ and $\tau_3$ can be readily 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 number of times the state of the electron needs to be switched to produce any desired rotation on the nuclear spins, in a given eigenstate in either $\alpha$ or $\beta$ manifold. The problem of finding the minimum number of switchings for producing arbitrary rotations by switching between two axis of rotation has been studied before. We recapitulate the main results and motivate further extensions.

**Remark 1 Uniform Generation:** Let $\gamma$ denote the angle between two rotation axis $d_\alpha$ and $d_\beta$ as shown in Fig. 3. Then it is a known result [19] that any three dimensional rotation in group $SO(3)$ (similar result holds for group $SU(2)$) can be constructed by not more that $k + 2$ rotations (performed around $d_\alpha$ or $d_\beta$), where

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

Therefore, starting in either $\alpha$ or $\beta$ manifold, any rotation on nuclear spin can be obtained by a pulse sequence as shown in Fig. 3 with no more that $k + 2$ evolution periods $\tau_i$. Furthermore, there exist algorithms to find the
sequence with minimum number of switches \[21\] to generate any arbitrary rotation using only rotations around \(d_\alpha\) and \(d_\beta\). Here, we present a strategy for obtaining such a sequence (which need not be minimal in terms of number of switches) which is easy to construct geometrically.

Let \(\tau_1 - \tau_k\) (\(k\) even) be the times for alternate rotations (starting with \(d_\beta\)) around \(d_\beta\) and \(d_\alpha\), with angular frequency \(\omega_\beta\) and \(\omega_\alpha\), so chosen that the resulting rotation takes the initial vector \(d_\alpha\) to unit direction \(\hat{n}\) as in figure (2B). Let

\[
U(\alpha, \tau) = \exp(-i\omega_\alpha \tau \ d_\alpha \cdot \sigma) \quad \text{and} \quad U(\beta, \tau) = \exp(-i\omega_\beta \tau \ d_\beta \cdot \sigma),
\]

be rotations in \(SU(2)\) around axis \(d_\alpha\) and \(d_\beta\). A rotation by angle \(\theta\) around an unit vector \(\hat{n} = n_x i + n_y j + n_z k\), takes the form

\[
\exp(-i\theta \hat{n} \cdot \sigma) = \cos \frac{\theta}{2} \mathbf{1} - i \frac{\theta}{2} \hat{n} \cdot \sigma,
\]

where \(\hat{n} \cdot \sigma = n_x \sigma_x + n_y \sigma_y + n_z \sigma_z\). Then, a sequence of rotations

\[
U(\alpha, \tau_k) \ldots U(\beta, \tau_1) U(\alpha, \tau) U(\beta, -\tau_1) \ldots U(\alpha, -\tau_k),
\]

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

\[
t_\alpha = \frac{2\pi}{\omega_\alpha}; \quad t_\beta = \frac{2\pi}{\omega_\beta};
\]

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

\[
U(\beta, t_\beta - \tau) = -U(\beta, -\tau); \quad U(\alpha, t_\alpha - \tau) = -U(\alpha, -\tau)
\]

Since \(k\) is even, the negative signs in (3) cancel out (if \(k\) is odd, it just produces a global phase). We now show how all these results need to be further generalized if one is interested in producing controlled operations on the nuclei.

A. Controlled Operations on Nuclear Spins

A \(\alpha\) manifold selective controlled operation on the nuclear spins transforms \(|\alpha\alpha\rangle \rightarrow |\alpha\alpha\rangle\) and \(|\alpha\beta\rangle \rightarrow |\alpha\beta\rangle\) and \(|\beta\alpha\rangle \rightarrow |\beta\alpha\rangle\) and \(|\beta\beta\rangle \rightarrow |\beta\beta\rangle\). While the \(\beta\) electron manifold is left unperturbed, i.e., \(|\beta\alpha\rangle \rightarrow |\beta\alpha\rangle\) and \(|\beta\beta\rangle \rightarrow |\beta\beta\rangle\). We show that such controlled operations can again be performed by toggling the state of the electron spin with \(\pi\) pulses, followed by suitable delays. This is best seen by observing that by flipping the state of the electron spins, we can switch between the effective Hamiltonians (generators)

\[
H_1 = \omega_I I_z + S_z (A I_z + B I_x)
\]

and

\[
H_2 = \omega_I I_z - S_z (A I_z + B I_x)
\]

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For example, the pulse sequence $\tau_1 - \pi - \tau_2 - \pi$ (where $\pi$ pulse is on the electron) evolves $H_1$ for time $\tau_1$ followed by $H_2$ for time $\tau_2$. 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 $\mathfrak{t} = -i\{I_x, I_y, I_z, S_zI_x, S_zI_y, S_xI_y\}$. Then a standard result on controllability 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

$$\exp(-i(aS_zI_\rho + bI_q)),$$

where $I_\rho$ and $I_q$ are nuclear spin operators can be synthesized. Specifically, we can perform a rotation $\exp(-iS_\alpha I_\gamma)$ that only rotates nuclei in the electron’s $\alpha$ manifold ($S_\alpha = (1/2 + S_z)$, $S_\beta = (1/2 - S_z)$).

We rewrite,

$$H_1 = \omega_1(S^\alpha_z + S^\beta_z)I_z + \frac{(S^\alpha_z - S^\beta_z)}{2}(AI_z + BI_x),$$

which when rewritten looks like

$$H_1 = S^\alpha_z(\omega_1I_z + \frac{(AI_z + BI_x)}{2}) + S^\beta_z(\omega_1I_z - \frac{(AI_z + BI_x)}{2}),$$

which written in a $6 \times 6$ matrix form takes the block diagonal form

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

where $D_\alpha$ denotes rotation around axis $d_\alpha$ with angular frequency $\omega_\alpha$ and $D_\beta$ denotes rotation around axis $d_\beta$ with angular frequency $\omega_\beta$. The algebra $\mathfrak{t}$ is simply all block diagonal $6 \times 6$ skew Hermitian matrices, i.e., matrices of the form $\begin{pmatrix} A_1 & 0 \\ 0 & A_2 \end{pmatrix}$, i.e. $A_1 = -A_1^\dagger$ and $A_2 = -A_2^\dagger$. Note, in the special case when $A = 0$ in Eq. 1, then $\omega_\alpha = \omega_\beta$ in Eq. 1.

In this special case the algebra generated by $H_1$ and $H_2$ is only 3 dimensional algebra and we cannot produce arbitrary controlled operations on the nuclei. This case however is of only theoretical interest and we will not consider it any further.

A $\pi$ pulse on the electron will switch $H_1$ to $H_2$ and vice-versa. A sequence of delays and flips $\tau_1 - \pi - \tau_2 - \cdots - \tau_k - \pi$, where $k$ is say even, will execute the following rotations on the nuclear spins in $\alpha$ and $\beta$ manifold 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 $\tau_k$, 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 \( \tau_k \), such that \( U_\beta = U_\alpha = U_f \) constitutes a uniform rotation on the nuclei. In general, we want to find a sequence that performs manifold selective operations, i.e., \( U_\alpha \) and \( U_\beta \) are as desired. It is also a known result [20] that there exists a finite number of switchings \( N \), such that arbitrary \( U_\alpha \) and \( U_\beta \) can be constructed by no more than \( N \) number of switchings. Finding methods to generate these in minimum number of switchings is an interesting problem. 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 \( \beta \) manifold (with \( k \) even) given by

\[
U_\beta = U(\beta, -\tau_1) \ldots U(\alpha, -\tau_k) U(\alpha, \tau_k) \ldots U(\beta, \tau_1),
\]

where \( U_\beta \) is implemented as

\[
U_\beta = U(\beta, t_\beta - \tau_1) \ldots U(\alpha, t_\alpha - \tau_k) U(\alpha, \tau_k) \ldots U(\beta, \tau_1).
\]

By definition, \( U_\beta = 1 \). We now have the independence in selecting \( \tau_1 - \tau_k \), in such a way that the corresponding rotation on the \( \alpha \) manifold, given by

\[
U(\alpha, t_\beta - \tau_1) \ldots U(\alpha, t_\alpha - \tau_k) U(\beta, \tau_k) \ldots U(\alpha, \tau_1) = U_F.
\]

We rewrite this relation as

\[
1 = U(\beta, \tau_k - t_\alpha) \ldots U(\alpha, \tau_1 - t_\beta) U_F U(\alpha, -\tau_1) \ldots U(\beta, -\tau_k),
\]

Equation (10), can then be written as,

\[
1 = BU(\beta, \tau_k) \ldots AU(\alpha, \tau_1) U_F U(\alpha, -\tau_1) \ldots U(\beta, -\tau_k),
\]

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

Equation (11) can be used to determine \( \tau_1 - \tau_k \). In equation (11), 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 \( 1 \)). These can be obtained iteratively in a closed form by the following optimization procedure. Suppose \( \tau_2 - \tau_k \) is fixed. Now the Eq. (11), can be written as

\[
Tr(U_F^k) = Tr(C U(\alpha, \tau_1) U_F U(\alpha, -\tau_1)),
\]

where the time \( \tau_1 \) is chosen to maximize \( Tr(U_F^k) \). This optimization then takes the form

\[
tr(CU(\alpha, \tau_1)U_FU(\alpha, -\tau_1)) = 2\{\cos \frac{\theta}{2} \cos \frac{\theta_c}{2} - \sin \frac{\theta}{2} \sin \frac{\theta_c}{2} \cdot n_\alpha \cdot n(\tau_1)\},
\]

where \( U_F = \exp(-i\theta n \cdot \sigma) \) and \( C = \exp(-i\theta_c n_\alpha \cdot \sigma) \).
In the above expression $\tau_1$ generates rotation around axis $d_\alpha$ and only rotates $n_\perp$, the part of $n$, that is perpendicular to $d_\alpha$. The above expression is maximized when $n_\perp$ is aligned or anti-aligned (depending on the sign of $\sin \frac{\theta}{2} \sin \frac{\theta_c}{2}$) with $(n_c)_\perp$, the part of $(n_c)$ that is perpendicular to $d_\alpha$. We can write an explicit expression for $\tau_1$. Let $a$ be a unit vector in the direction of $\sin \frac{\theta}{2}(n - (n \cdot d_\alpha)d_\alpha)$, and $b$ be a unit vector in the direction of $\sin \frac{\theta}{2}(n_c - (n_c \cdot d_\alpha)d_\alpha)$, then $\sin(\tau_1) = (b \times a) \cdot d_\alpha$. Having determined the optimal value $\tau_1$, we can now proceed to maximize $\tau_2$ which is now an optimization of a function like $\text{Tr}(C_1 U(\beta, \tau_2) U^1_F U(\beta, -\tau_2))$, and so on. Having found a set of values $\tau_1 - \tau_k$, this way, we iterate again. Each iteration increases the value of $\text{tr}(U^k_F)$, and therefore this value stabilizes to a limit. If this value is not 2, we can increase $k$ and repeat the iteration. The resulting set of evolution times $\tau_1 - \tau_k$ synthesize a selective rotation on the $\alpha$ manifold as in Eq. (9). Similarly we can synthesize a selective rotation on the $\beta$ manifold and therefore any rotation of the kind given in Eq. (8). Alternatively, we can synthesize a desired unitary transformation $U_\beta$ on the beta manifold as described in Eq. (4), which results in some rotation $U'_\alpha$ on the alpha manifold (that is easily computed). Now performing an $\alpha$ manifold selective rotation of $U_\alpha(U'_\alpha)^{-1}$, will result in the the desired rotations on the two manifolds. Using the above described method, we explicitly compute the pulse sequence for implementing a controlled rotation $\exp(-i \pi S^\alpha I_z)$, which inverts the nuclear spins in the $\alpha$ manifold and leaves the $\beta$ manifold unaffected. We assume $\frac{\omega_1}{4} = .5$ and $\frac{\omega_2}{4} = 1$. This gives $t_\alpha = 4\pi$ and $t_\beta = \frac{4\pi}{\sqrt{5}}$. The pulse sequence

$$\tau_1 - \pi - \tau_2 \ldots \tau_5 - \pi - t_\alpha - \pi - (t_\beta - \tau_5) - \pi - (t_\alpha - \tau_4) - \ldots - \pi - (t_\beta - \tau_1).$$

where the switching times, in the units of $1/A$ are $\tau_1 = 10.32$, $\tau_2 = 4.64$, $\tau_3 = 9.75$, $\tau_4 = .2760$, $\tau_5 = 10.97$ and $\tau_6 = 5.47$, implements the desired rotation. Also note that using the above sequence as a building block, the pulse sequence $P - \pi - P - \pi$ implements the rotation $\exp(-i \pi I_x)$. Similarly we can find a switching sequence $Q$, that implements $\exp(-i \pi I_x)$. Then the pulse sequence $P - Q - P - Q$ will implement the rotation $\exp(-i \pi 2I_z S_z)$.

**Remark 2 (Synthesizing Arbitrary Unitary Transformations:)** Any unitary transformation on the electron-nuclear spin system is given by $U_1 U_S \exp(-i[aS_x I_x + bS_y I_y + cS_z I_z]) V_I V_S$

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, $I_x S_x, I_y S_y, I_z S_z$ all commute.

As described in Eq. (8), we have shown that all rotations of the kind $\exp(-i \theta_1 S_z I_a)$ and $\exp(-i \theta_2 I_b)$ 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, $\exp(-i \theta_3 S_y)$ on the electron can be used to perform arbitrary unitary rotation on the electron-nuclear spin system. The bilinear rotations $\exp(-i \theta S_y I_x)$ can be synthesized as

$$\exp(-i \theta S_y I_x) = \exp(-i \frac{\pi}{2} S_y) \exp(-i \theta S_z I_x) \exp(i \frac{\pi}{2} S_y).$$
Remark 3 (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 techniques. For \( k \) even, let \( \tau_1 - \pi - \tau_2 - \cdots - \tau_k - \pi \), be a sequence that implements the propagator \( U_f = \exp(-i\frac{\tau}{2}I_q) \). Then the sequence \( P - P \), where \( P = \tau_1 - \pi - \tau_2 - \cdots - \tau_k \), will implement the propagator \( \exp(-ibI_q) \) and refocus all resonance effects.

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 \( \exp(-i\pi I_q) \) compensating for offset effects and a switching sequence (assuming no resonance offset), \( Q = \tau_1 - \pi - \tau_2 - \cdots - \tau_k \), such that \( k \) is even and \( Q - \pi \) implements \( \exp(-i\frac{\pi}{2}S_zI_p) \). Then the sequence \( Q - R - Q - R \) will implement the desired propagator \( \exp(-iaS_zI_p) \) and compensate for offset effects on the electron.

Remark 4 (Polarization Transfer from Electron to Nucleus:) The above described methods can now be used to transfer polarization from electrons to the nucleus. The desired transformation

\[
S_z \to I_z,
\]
can be performed as follows.

\[
S_z \xrightarrow{\exp(-i\frac{\pi}{2}S_y)} S_z \xrightarrow{\exp(-i\frac{\pi}{2}S_y I_y)} 2S_y I_y \xrightarrow{\exp(-i\frac{\pi}{2}S_y)} 2S_z I_z \xrightarrow{\exp(-i\frac{\pi}{2}S_y I_y)} I_z, \tag{13}
\]

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

Remark 5 (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

\[
H_0 = \Omega S_z + \sum_{j=1}^{N} \omega_{ij} I_{jz} + S_z \sum_{j=1}^{N} (A_j I_{jz} + B_j I_{jz}).
\]

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

\[
H_1 = \sum_{j=1}^{N} \omega_{ij} I_{jz} + S_z \sum_{j=1}^{N} (A_j I_{jz} + B_j I_{jz}); \quad H_2 = \sum_{j=1}^{N} \omega_{ij} I_{jz} - S_z \sum_{j=1}^{N} (A_j I_{jz} + B_j I_{jz}),
\]

span the space \( \{I_{jp}, S_z I_{jq}\} \). Therefore any rotation on the individual nuclei is achievable by simply switching the electron state by \( \pi \) pulses. These rotations combined with rotations on the electron are sufficient to synthesize any unitary transformation on the coupled electron-nuclear spin system. Let \( U_{\alpha j} \) and \( U_{\beta j} \) represent the desired unitary transformation on the \( \alpha \) and \( \beta \) manifold of the \( j^{th} \) nuclei. Let \( \tau_1 - \pi - \cdots - \pi - \tau_k - \pi \), \( (k \text{ even}) \) be the pulse sequence
that implements such a transformation. Then the switching times can be computed by iterative maximization over \( \tau_1 - \tau_k \), of a trace function like

\[
\sum_j tr(U'_{\alpha_j}U(\beta_j, \tau_k) \cdots U(\alpha_j, \tau_1)) + tr(U'_{\beta_j}U(\alpha_j, \tau_k) \cdots U(\beta_j, \tau_1)),
\]

where \( U(\alpha_j, \tau) \) represents rotation of the \( j^{th} \) nuclei around the axis \( \alpha_j \), with angular frequency \( \omega_{\alpha_j} \) for time \( \tau \).

Gradient algorithms for maximization of such trace functions were presented in \[24\].

III. CONCLUSION

In this article, we developed new techniques for control of coupled electron-nuclear spin system. We showed that the spin system at magnetic field strengths where the Larmor frequency of the nucleus is comparable to the hyperfine coupling strength can be controlled by simply performing a sequence of flips (each followed by a suitable delay) on 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, the switched mode control can be used to synthesize any unitary transformation on 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. 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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