Meridional composite pulses for low-field magnetic resonance

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ABSTRACT
We discuss procedures for error-tolerant spin control in environments that permit transient, large-angle reorientation of magnetic bias field. Short sequences of pulsed, non-resonant magnetic field pulses in a laboratory-frame meridional plane are derived. These are shown to have band-pass excitation properties comparable to established amplitude-modulated, resonant pulses used in high, static-field magnetic resonance. Using these meridional pulses, we demonstrate robust z inversion in proton (1H) nuclear magnetic resonance near earth’s field.

I. INTRODUCTION
Pulsed alternating (ac) electromagnetic fields are a staple of atomic, electronic and nuclear spin resonance spectroscopies. Following decades of development in these disciplines and others, e.g., magnetic resonance imaging (MRI) and quantum information processing (QIP), there exist many species of ac pulse for precise qubit control that compensate for errors inevitably present in experimental parameters. Among error-tolerant pulses engineered are those utilizing discrete phase-shifting, amplitude modulation or both amplitude-and-phase modulation of the ac fields. These pulse composition strategies are available to traditional spin-resonance experiments, which are performed inside strong magnets (e.g., superconducting magnets) with fixed magnitude and direction of the magnetic field. In this scenario, only ac amplitude and phase degrees of freedom remain for spin control. Other strategies are in principle possible, however. At a mathematical level, error-compensated pulse design can be traced to a common set of principles, for instance the Magnus expansion, impulse-response theory, recursive iteration and other time symmetry considerations.

When the strong field constraint is removed, new pulse strategies become available, and existing pulse strategies can be implemented using different degrees of freedom. In this paper we illustrate the above re-utilization concept to derive error-tolerant pulses for magnetic resonance experiments where orientation of total magnetic field is unconstrained in the laboratory frame of reference. The case includes Earth’s field nuclear magnetic resonance (NMR) as well as the emerging area of zero and ultralow-field (ZULF) NMR, which presents attractive regimes for nuclear spin hyperpolarization, relaxometry and precision spectroscopy in fields ranging from nT to µT. Here, standard ac pulses may achieve spin-species and/or transition-selective excitation. Optimal control pulses and direct-current (dc) analogs of ac composite pulses (e.g., 90x180x90x) can also be used for error compensation.

We observe that composite pulses do not always appear to translate directly from ac (high-field) to dc (low-field) techniques. For instance, in high field, a 90x180,90x pulse is often a first choice for tolerance to error in Rabi frequency and thus pulse length. However, in low-field, the pulse length tolerance of a dc composite pulse can be achieved using analogs of ac pulses that compensate for offset in the ac carrier frequency – a different source of error. This concept shall be illustrated for dc composite pulses where fields are confined to a single meridional plane of the Bloch sphere (e.g., z plane, where z defines the bias axis). We call such pulses meridional composite pulses, and show that they are considerably more selective than traditional composite pulses, including 90x180,90x where magnetic field is kept in the equatorial plane of the Bloch sphere (xy plane).

II. THEORY
In any NMR scenario, the magnetic field \( \mathbf{B}(t) \) is used to produce controlled rotations of a spin \( \mathbf{S} \), governed by the Bloch equation

\[
\frac{d}{dt} \mathbf{S} = \gamma \mathbf{S} \times \mathbf{B}.
\]

(1)

In a high-field NMR scenario, a strong constant field along the z direction with magnitude \( B_0 \) is applied, and a weaker orthogonal field \( B_{\parallel}(t) \) is temporally shaped to produce pulses of oscillating field near the Larmor frequency \( \omega_L = \gamma B_0 \), with a determined detuning, duration a)

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and phase. Via the Bloch equation, such a pulse produces a spin rotation $R(\psi, \vec{n})$, where the spin rotation angle $\psi$ is proportional to the strength and duration of the pulse, and the (rotating frame) rotation axis $\vec{n}$ is determined by the phase and frequency of the pulse.

In low-field NMR, it is possible to directly implement a rotation $R(\psi, \vec{n})$ about a (laboratory frame) axis $\vec{n}$, by applying a dc field of strength $B$ along $\vec{n}$ for a time $\tau$, to generate rotation by an angle $\psi = \gamma B \tau$. Rotations with arbitrary $\vec{n}$ and $\psi$ can in principle be produced with three-axis control of $\vec{B}(t)$. In this way, any simple rotation $R(\psi, \vec{n})$ used in high-field NMR can be implemented also in low-field NMR.

Composite pulses are not simple pulses, but rather trains of simple pulses that together implement a desired rotation. Unlike simple pulses, these can be designed to perform nearly the same rotation for a range of parameter values, e.g., $\gamma$ or $B_0$, so these rotations become robust against experimental imperfections. They can also be used to apply different rotations to different $\gamma$ values, and thus implement species-specific rotations. Composite pulses do not translate directly from high-field to low-field techniques, because parameter variations affect the rotation in different ways. For example, in a resonant rotation, $\vec{n}$ depends on the detuning and thus on $\gamma$, whereas for a dc rotation it is $\psi$ that depends on $\gamma$.

As a starting point for meridional composite pulse design we use the theorem that successive rotation of a spin (and more generally, any 3d object) by $\pi$ radians about an arbitrary pair of unit vectors $\vec{n}'$ and $\vec{n}''$, where $\phi/2$ is the angle between $\vec{n}'$ and $\vec{n}''$, i.e. $\vec{n}' \cdot \vec{n}'' = |\vec{n}'||\vec{n}''|\cos(\phi/2)$:

$$R(\pi, \vec{n}')R(\pi, \vec{n}'') = R(\phi, \vec{n}).$$

By extension, an equation follows for the cumulative effect of $2N$ rotations-by-$\pi$ axes $\vec{n}_1', \vec{n}_2', \vec{n}_2', \ldots, \vec{n}_N', \vec{n}_N''$ in a common plane normal to $\vec{n}$:

$$\prod_{j=1}^{N} R(\pi, \vec{n}_j') R(\pi, \vec{n}_j'') \approx R(\sum_{j=1}^{N} \phi_j, \vec{n}).$$

For instance, if all of the $\vec{n}'$ and $\vec{n}''$ vectors lie within the Cartesian $xz$ plane as defined by vectors $\vec{x} = (1, 0, 0)$ and $\vec{z} = (0, 0, 1)$, then the overall rotation is produced about the $y$ axis, defined $\vec{y} = (0, 1, 0)$; $\vec{n} = \vec{y}$.

The problem of interest for robust, spin-selective pulse generation is the approximate implementation of Eq. (3), whereas a sequence of $2N$ rotations by $\kappa\pi$ by $\kappa\pi$ is applied about axes $\vec{n}_1', \vec{n}_2', \ldots, \vec{n}_N', \vec{n}_N''$. If, as above, the angle between $\vec{n}_j'$ and $\vec{n}_j''$ is $\phi_j/2$, the objective is to find a sequence of angles $\phi_1, \phi_2, \ldots, \phi_N$ such that the resulting rotation is

$$\tilde{R}(\kappa) \equiv \prod_{j=1}^{N} R(\kappa\pi, \vec{n}_j') R(\kappa\pi, \vec{n}_j'') \approx R(\beta, \vec{n}).$$

for some detuned range of $\kappa$, (and therefore gyromagnetic ratio, $\gamma \propto \kappa$), say $(\kappa \mod 2) = (1 + \delta)$, where $\delta$ is the detuning. Here $\beta$ is the target rotation angle.

One route to a solution is to recognize that for $\kappa = (1 + \delta)$ one can cast Eq. (4) (see Appendix A) into a form

$$\tilde{R}(\kappa) = \prod_{j=1}^{N} R \left( \frac{\phi_j}{2}, \vec{y} \right) R(\pi[1 + \delta], \vec{z}) R \left( -\frac{\phi_j}{2}, \vec{y} \right) R(\pi[1 + \delta], \vec{z})$$

$$= R_z^N \prod_{j=1}^{N} \left[ R_z^2(\delta) R(\frac{\phi_j}{2}, \vec{y}) \right] \left[ R_z^{2N - 1}(\delta) R \left( -\frac{\phi_j}{2}, \vec{y} \right) \right].$$

(5)

where $R_z^d(\delta)$ is the $d$th power of the right-acting superoperator $R_z(\delta)$, which rotates operators $R(\phi, \vec{n})$ by an angle $\pi(1 + \delta)$ about $z$, as defined by $R_z(\delta) R(\phi, \vec{n}) = R(\pi[1 + \delta], \vec{z}) R(\phi, \vec{n}) R(\pi[1 + \delta], \vec{z})$. The form of Eq. (5) indicates that, relative to the ideal transformation ($\kappa = 1$), the error $\delta$ has the effect of shifting the spins’ frame of reference by an offset $\delta \approx 2\phi$ about $\vec{z}$ between each $\phi_j$ rotation. In this way, the problem of finding a suitable set of $\phi_j$s is mapped onto another problem; that of compensating for frame offset. Frame-offset compensation is a well-explored topic in physics, and of high importance in NMR, MRI and QIP. One representative strategy uses broadband uniform-rotation pure-phase (BURP) pulses, as first developed by Geen and Freeman. A BURP pulse is an amplitude-modulated ac pulse of duration $\tau_p$, with the carrier resonant with the nominal Larmor frequency. The carrier envelope is chosen such that for detuning $\delta = 0$, the (rotating frame) rotation is $R(\beta(t), \vec{y})$, where for $0 \leq t \leq \tau_p$ the accrued flip angle is

$$\beta(t) = a_0 \frac{t}{\tau_p} + b_0 + \sum_{k=1}^{n_{\text{cut}}} \left[ a_k \sin \left( \frac{2\pi k t}{\tau_p} \right) + b_k \cos \left( \frac{2\pi k t}{\tau_p} \right) \right].$$

(6)

This is a truncated Fourier series, and a cutoff of $n_{\text{cut}} \approx 5$ typically gives sufficient precision [12,13]; numerical values for $a_k$ and $b_k$ are given in the Supplemental Material. BURP pulses generally tolerate mismatch between the carrier and Larmor precession frequencies, with an excitation pass-band inversely proportional to the BURP pulse length.

Using dc pulse pairs as described in Eq. (3), we can make a pointwise approximation of $\beta(t)$: We define intermediate rotation angles

$$\phi_j = \beta \left( \frac{\tau_p j}{N} \right) - \beta \left( \frac{\tau_p (j - 1)}{N} \right),$$

(7)

and then construct a sequence of nominally-$\pi$ rotations

$$R(\kappa) = \prod_{j=1}^{N} R(\kappa\pi, \vec{n}_j') R(\kappa\pi, \vec{n}_j'')$$

(8)

with $\vec{n}_j' = (\pm \sin(\phi_j/4), 0, \cos(\phi_j/4))$ and $\vec{n}_j'' = (-\sin(\phi_j/4), 0, \cos(\phi_j/4))$. This defines a meridional composite pulse, i.e., a series of $\kappa\pi$ rotations about pairs of axes in the $xz$ plane, separated by angles $\phi_j/2^{16}$. 


κ as defined in Eq. (9). Dashed vertical lines show values of torsional (of flip angle accumulated in the xz plane for the conventional (β, black) and discretized (φj, red) pulses with N = 1, 2, 4, 10, 20, 40. Plots to the right show z inversion performance $\tilde{R}_{zz}(\kappa)$ for the discretized pulse, using scaling factors $s = 1$ (red), $s = 0.9$ (gray), $s = 1.1$ (light gray) as defined in Eq. (9). Dashed vertical lines show values of $\kappa(S)/\kappa(1^\text{H}) \equiv \gamma_z/\gamma_H$, for the case $\kappa(1^\text{H}) = 1$.

Performance of the discretized BURP pulses can be analyzed by numerical simulation. As a first example, we study the inversion pulse I-BURP-1, as shown in Fig. 1. Continuous and pointwise $\beta(t)$ values agree closely with one another for $N \gtrsim n_{\text{max}}$. For instance, for $N > 10$, the fractional difference between $\beta(t)$ and the connecting line between sampling points $\beta(jT_p/N)$ is below 0.05 for all time points.

We quantify the inversion by $\tilde{R}_{zz}(\kappa) = \vec{z}^T \tilde{R}(\kappa) \vec{z}$, where $\tilde{R}(\kappa)$ is the matrix representation of the net rotation operator $\tilde{R}(\kappa)$. A value $\tilde{R}_{zz}(\kappa) = -1$ implies complete spin inversion, while $\tilde{R}_{zz}(\kappa) = +1$ indicates zero net rotation of the spin away from $\vec{z}$. From plots on the right side of Fig. 1, $\tilde{R}_{zz}(\kappa)$ shows an inversion passband of full width at half-maximum $2\delta \approx 5/N$, which for moderate values $N \sim 20$ should be wide enough to provide generous error tolerance, e.g., $2\delta \sim 0.25$, while being selective in $\gamma$.

DC field pulses are typically produced by field coils, with each coil contributing the field component along one Cartesian axis. To implement the pulse sequence of Eq. (5), for example, X (field along $\vec{x}$) and Z (field along $\vec{z}$) coils could be used. We now analyze the effect of a mis-calibration of the Z coil by a factor $s$, so that the produced field is

$$\vec{B} = B_0(\sin \varphi, 0, s \cos \varphi),$$

where $B_0$ is the intended field strength and $\varphi$ is the intended angle in the $xz$ plane. For $s \approx 1$, the effect on the rotation angle, i.e. on $\delta$, is first order in $s - 1$, and the effect on $\vec{n}$ is a non-simple function of $\varphi$ and $\phi$. For symmetric displacement of $\vec{n}'$ and $\vec{n}$ about $\vec{z}$ (and thus $\vec{n}' + \vec{n}$ parallel to $\vec{z}$, when $\varphi = \pm \phi/2$) the excitation profile remains mostly unchanged with respect to $s$ and the passband center shifts to $\kappa = (1 + s)/2$. Representative profiles for the I-BURP-1 pulse are shown in Fig. 1.

Another result of this approach is dc analogs of wide-offset-tolerant ac composite pulses. These pulses in high-field NMR are often termed “phase-alternating composite pulses” due to the alternating sign of flip angle in the ac frame, e.g., $(\beta_1, \beta_2, \beta_3) = (59^\circ, -298^\circ, 59^\circ)$. The flip angles can be directly mapped to a dc meridional composite pulse using $\phi_j = \beta_j$.

Selected phase-alternating composite pulses for inversion and the widths of their passbands are listed in Table I. Highly uniform inversion can be achieved using only a few pulses ($N < 10$), with a degree of selectivity comparable to, if not better than I-BURP-1. We note that the passband widths vary between the works of different authors because of different optimization criteria. Uniform excitation within the passband is often given the highest priority, followed by rejection in stopband. Because in some low-field NMR applications both figures of merit may have equal priority, the present work includes some additional solutions. The original sequences we report in Table I are found in a few minutes with a standard desktop computer, by randomly sampling ~ 50000 points in a $N - 1$ dimensional space of $\phi$ values $\phi_1, \phi_2, \ldots, \phi_{N-1}$, with resolution $0.02 \times \pi$ rad. The final angle is constrained to be $\phi_N = \pi - \sum_{j=1}^{N-1} \phi_j$, so that $\beta = \pi$. Our merit function is $l_1 + l_2$, where $l_1$ is the mean value of $(1 + \tilde{R}_{zz}(\kappa))^2$ over the range $0.8 < \kappa < 1$ and $l_2$ is the mean of $(1 - \tilde{R}_{zz}(\kappa))^2$ for $|\kappa| < 0.5$. Angle sets up to length $N = 9$ giving widest passband and stop-
band widths are presented in Table I. Generally, we observe these sequences can have a wider passband than the existing phase-alternating composite pulses of the same length $N$. An increased width of the stopband is more challenging and requires higher $N$. The performance of these pulses is illustrated in Fig. 2.

### III. EXPERIMENTAL RESULTS

The band-pass profiles of meridional composite pulses such as those shown in Fig. 1 and Fig. 2 can be measured using a sample containing only a single spin species, e.g. $^1$H in water ($^1$H$_2$O). We note that the rotation axes $\mathbf{n}'$ and $\mathbf{n}''$ are independent of $\gamma$, while $\kappa$ is directly proportional to $\gamma$ and pulse duration Thus the effects of a change in $\gamma$ can be simulated by a corresponding change in the pulse duration.

The experimental setup and testing protocol are shown in Fig. 3a. Water, pre-polarized along $z$, flows through a cell surrounded by two coils (X and Z) that produce uniform fields along $\mathbf{x}$ and $\mathbf{z}$, respectively. Bipolar current control of the X coil is provided by a simple electronic circuit comprising a digital-to-analog converter, amplifier and H-bridge module. A constant current is passed through the Z coil, as in Fig. 3b (right). In this arrangement (unlike what is suggested by Eq. (9)), the field strength $B_0$ depends on the angle $\phi$. The pulse duration $\tau$ is compensated accordingly, so that the nominal rotation angle $\psi = \gamma B_0 \tau$ is always $\pi$. Further details are given in the Methods section.

The performance of the spin-selective inversion pulses is measured by applying a composite pulse, then immediately applying a dc pulse of flip angle $90^\circ$ along $+\mathbf{x}$. The peak field of the composite pulse is controlled such that I-BURP-1 pulse lengths are of comparable length for different $N$: $(\tau_p/\kappa) \sim 8$ ms for $^1$H. An alkali-metal-vapor magnetometer adjacent to the flow cell detects the resulting $^1$H free precession signal (FID).

The observed FID amplitude for composite pulses of duration $\kappa \tau_p$ is denoted $S_\kappa$, and the FID amplitude with no applied composite pulse is $S_0$. The ratio $S_\kappa/S_0$ equals $\hat{R}_{zz}(\kappa)$, which takes values between $-1$ (for complete spin inversion) and $+1$ (for no spin inversion) and is plotted up to $\kappa = 4$ for various pulses in Fig. 4.

The experimental and simulated profiles agree closely, with residuals below the experimental error margins. This result confirms that spin selective pulses can indeed be designed using the approach of Eq. (3). It also suggests that any imperfections in the pulses are small compared to the compensation limits, which is remarkable considering the simplicity of the electronic drive circuitry.

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**Table I.** Composite pulses for the inversion operation $z \to -z$. All angles $\phi_j$ are given in degrees.

| $N$ | $\phi_1$ | $\phi_2$ | $\phi_3$ | $\phi_4$ | $\phi_5$ | $\phi_6$ | $\phi_7$ | $\phi_8$ | $\phi_9$ |
|-----|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 2   | 55       | -235     |          |          |          |          |          |          |          |
| 3   | 59       | -298     | 59       |          |          |          |          |          |          |
| 3   | 24       | -97      | 253      |          |          |          |          |          |          |
| 4   | -34      | 123      | -198     | 289      |          |          |          |          |          |
| 4   | 27       | -81      | 263      | -30      |          |          |          |          |          |
| 5   | 325      | -263     | 56       | -263     | 325      |          |          |          |          |
| 9   | 70       | -238     | -355     | 296      | 276      | 296      | -355     | -238     | 70       |

| $|\kappa| < 0.20$ | $0.83 < \kappa < 1.17$ | this work |
| $|\kappa| < 0.36$ | $0.93 < \kappa < 1.07$ | Shaka et al. |
| $|\kappa| < 0.24$ | $0.75 < \kappa < 1.25$ | this work |
| $|\kappa| < 0.29$ | $0.86 < \kappa < 1.14$ | Shaka et al. |
| $|\kappa| < 0.29$ | $0.75 < \kappa < 1.25$ | this work |
| $|\kappa| < 0.29$ | $0.95 < \kappa < 1.05$ | Shaka et al. |
| $|\kappa| < 0.55$ | $0.89 < \kappa < 1.11$ | this work |

Figure 2. Spin vector trajectories in the Bloch sphere and band-pass inversion profiles for selected composite pulses listed in Table I. The black, blue, and red trajectories are for values $\kappa = 0.3$, $\kappa = 0.85$ and $\kappa = 1.0$. Rotation axes indicated by yellow arrows are displaced symmetrically about $\mathbf{z}$ in the $xz$ plane. The solid red curve indicates the band-pass profile $\mathbf{z} \to -\mathbf{z}$ for $s = 1$; dashed and dotted gray curves correspond to profiles for $s = 0.9$ and $s = 1.1$, respectively.
The composite pulse (Eq. (3)) is not limited to special an-
the criterion determining total flip angle of a meridional
strengths. As shown, this allows a single composite pulse
flip angle and axis are both determined by the dc field
effects on the generated spin rotations, in low-field NMR
fections of the experimental system and have different
offsets and flip-angle offsets originate in distinct imper-
In contrast to high-field NMR, where phase/frequency
offsets and flip-angle offsets originate in distinct imper-
fections of the experimental system and have different
effects on the generated spin rotations, in low-field NMR
flip angle and axis are both determined by the dc field
strengths. As shown, this allows a single composite pulse
strategy to be robust against variations of each, someth-
ing that is uncommon in high-field composite pulses.

Also unlike many high-field NMR composite pulses,
the criterion determining total flip angle of a meridional
composite pulse (Eq. (3)) is not limited to special an-
gles (e.g., 90°, 180°) and thus should allow one to ob-
tain pulses of arbitrary flip angle. This general design
approach, coupled with the above error compensation
properties, should prove valuable in spin resonance ap-
plications at low field that require robust and selective
control. The pulses demonstrated here are much shorter
in duration than high-frequency ac pulses of equivalent
compensation bandwidth, such as swept-frequency adia-
batic inversion pulses, and can be performed without
tuned high-frequency circuity. Application is expected
in sub-MHz NMR spectroscopy and MRI, field-cycling re-
 laxation measurements, nuclear spin polarimetry, as well
as portable NMR spectrometers for use outside of the
research laboratory.

The pulse durations τp in the present study are lim-
ited by hardware timer resolution (2 μs) and the field-
to-current ratio of the X coil. Faster clock speeds and
stronger fields could shorten pulse lengths by at least one
order of magnitude, giving τp between 10 μs and 100 μs.
These durations are much shorter than the periods of the
spin-spin scalar couplings between common nuclear spin
species, and thus should be applicable to heteronuclear
quantum control in low-field NMR, in which pulses selec-
tively rotate one or more spins in a multi-species system.
The selectivity and error tolerance should be complemen-
tary to existing control methods based on equatorial com-
posite pulses..

**METHODS**

Experimental testing of the composite pulses utilized a
continuous-flow (a.k.a. “polarization on tap”) test sample
for high-throughput measurement. As shown in Fig. 3a,
distilled water from a reservoir of several liters capacity
drained continuously under gravity (flow rate ∼1 mL s⁻¹)
through a low-homogeneity 1.5 T magnet to produce
the ¹H spins to reach thermal equilibrium polarization.
The liquid subsequently flowed into the ∼1 mL sample cham-erry, with the sample magnetization of around 1 pT being
aligned parallel to the axis of the background field, along 

Centered on the sample chamber was a solenoid coil
(∼7.5 mT/A) and a saddle coil (∼80 μT/A) to produce
magnetic fields along \( \vec{z} \) and \( \vec{x} \), respectively. Currents ap-
p lied to the saddle coil were controlled using a simple dc
switch comprising a microcontroller (ARM Cortex M4F)
digital-to-analog converter (12 bits, 0 to 3.3 V), oper-
ational amplifier (L272M, STMicroelectronics) and an H-
bridge module (Texas Instruments DRV8838 on Pololu
2990 carrier board), as shown in Fig. 3a. Rabi curves
were measured for different values of the DAC output
to confirm a linear output of voltage across the coils be-
tween 0.4 and 10 V (See Supplemental Material). This
determined the switchable range of field for a given series
resistance of the coil. The 10 V and ground op-amp rails
were connected to a standard laboratory power supply unit (Hameg HM7042-5).
Figure 4. Experimental (black circles) vs. simulated (solid red curves) band-pass inversion profiles for meridional composite pulses with $N = 2, 3, 4$ listed as “this work” in Table I and for discrete I-BURP-1 pulses with $N = 10, 12, 14, 16, 18, 20$ and $40$. Each data point represents the mean signal amplitude of approximately 10 NMR transients.

Details of magnetometer used to measure the NMR signals can be found in previous work\textsuperscript{27}. The signals $S_x$ and $S_0$ of the two pulse sequences are acquired in an interleaved fashion to minimize the effect of drifts.

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AUTHOR CONTRIBUTIONS

MCD Tayler made the theoretical interpretation and wrote the manuscript with input from all authors. S. Bodenstedt built the experimental apparatus, measured and analyzed the experimental data. MCD Tayler and MW Mitchell supervised the overall research effort.

COMPETING INTERESTS

There are no competing interests to declare.
REFERENCES

1M. A. Bernstein, K. F. King, and X. J. Zhou, Handbook of MRI pulse sequences (Academic Press, San Diego, CA, 2004) ISBN: 978-0-12-092861-3.

2R. de Graaf, In Vivo NMR Spectroscopy: Principles and Techniques (Wiley, 2019).

3D. Esteve, J.-M. Raimond, and J. Dalibard, Quantum entanglement and information processing, École d’été de physique théorique, session LXXIX, Les Houches (Elsevier Science, London, England, 2003) ISBN: 978-0444517289.

4J. A. Jones, “Quantum computing with NMR,” Progress in Nuclear Magnetic Resonance Spectroscopy 59, 91–120 (2011).

5A. Shaka and R. Freeman, “Composite pulses with dual compensation,” Journal of Magnetic Resonance (1969) 55, 487–493 (1983).

6M. H. Levitt, “Composite pulses,” Progress in Nuclear Magnetic Resonance Spectroscopy 18, 61–122 (1986).

7S. Wimperis, “Broadband, narrowband, and passband composite pulses for use in advanced NMR experiments,” Journal of Magnetic Resonance, Series A 109, 221–231 (1994).

8M. H. Levitt, “Composite pulses,” eMagRes (2007), 10.1002/9780470034590.emrstm0086.

9G. Demeter, “Composite pulses for high-fidelity population inversion in optically dense, inhomogeneously broadened atomic ensembles,” Physical Review A 93, 023830 (2016).

10A. Shaka, “Composite pulses for ultra-broadband spin inversion,” Chemical Physics Letters 120, 201–205 (1985).

11A. Shaka and A. Pines, “Symmetric phase-alternating composite pulses,” Journal of Magnetic Resonance (1969) 71, 495–503 (1987).

12H. Geen and R. Freeman, “Band-selective radiofrequency pulses,” Journal of Magnetic Resonance (1969) 93, 93–141 (1991).

13H. Freeman, “Shaped radiofrequency pulses in high resolution NMR,” Progress in Nuclear Magnetic Resonance Spectroscopy 32, 59–106 (1998).

14N. Khaneja, T. Reiss, C. Kehlet, T. Schulte-Herbrüggen, and S. J. Glaser, “Optimal control of coupled spin dynamics: design of NMR pulse sequences by gradient ascent algorithms,” Journal of Magnetic Resonance 172, 296–305 (2005).

15W. S. Warren and S. M. Mayr, “Shaped pulses,” eMagRes (2007), 10.1002/9780470034590.emrstm0493.

16I. D. Haller, D. L. Goodwin, and B. Luy, “SORDOR pulses: expansion of the Böhlen-Bodenhausen scheme for low-power broadband magnetic resonance,” Magnetic Resonance 3, 53–63 (2022).

17A. Brinkmann, “Introduction to average Hamiltonian theory. I. Basics,” Concepts in Magnetic Resonance Part A 45A, e21414 (2016).

18M. Shinnar, L. Bolinger, and J. S. Leigh, “The use of finite impulse response filters in pulse design,” Magnetic Resonance in Medicine 12, 81–87 (1989).

19M. H. Levitt and R. R. Ernst, “Composite pulses constructed by a recursive expansion procedure,” Journal of Magnetic Resonance (1969) 55, 247–254 (1983).

20S. Appelt, H. Kühn, F. W. Häising, and B. Blümich, “Chemical analysis by ultrahigh-resolution nuclear magnetic resonance in the earth’s magnetic field,” Nature Physics 2, 105–109 (2006).

21P. T. Callaghan, A. Coy, R. Dykstra, C. D. Eccles, M. E. Halse, M. W. Hunter, O. R. Mercer, and J. N. Robinson, “New zealand developments in earth’s field NMR,” Applied Magnetic Resonance 32, 63–74 (2007).

22C. A. Michal, “Low-cost low-field NMR and MRI: Instrumentation and applications,” Journal of Magnetic Resonance 319, 106800 (2020).

23J. W. Blanchard and D. Budker, “Zero- to ultralow-field NMR,” eMagRes, 1395–1410 (2016).

24M. C. D. Taylor, T. Theis, T. F. Sjolander, J. W. Blanchard, A. Kentner, S. Pustelnik, A. Pines, and D. Budker, “Invited review article: Instrumentation for nuclear magnetic resonance in zero and ultralow magnetic field,” Review of Scientific Instruments 88, 091101 (2017).

25K. F. Sheberstov, L. Chuchkova, Y. Hu, I. V. Zhukov, A. S. Kiyrutin, A. V. Eshtukov, D. A. Cheshkov, D. A. Barskiy, J. W. Blanchard, D. Budker, K. L. Ivanov, and A. V. Yurkovskaya, “Photochemically induced nuclear magnetic polarization of heteronuclear singlet order,” The Journal of Physical Chemistry Letters 12, 4686–4691 (2021).

26E. V. Dyke, J. Eills, R. Picazo-Frutos, K. Sheberstov, Y. Hu, D. Budker, and D. Barskiy, “Relayed hyperpolarization for zero-field nuclear magnetic resonance,” ChemRxiv (2022), 10.26434/chemrxiv-2022-1njs9.

27S. Bodenstedt, M. W. Mitchell, and M. C. D. Taylor, “Fast-field-cycling ultralow-field nuclear magnetic relaxation dispersion,” Nature Communications 12, 4041 (2021).

28S. Bodenstedt, D. Moll, S. Glöggler, M. W. Mitchell, and M. C. D. Taylor, “Decoupling of spin decoherence paths near zero magnetic field,” The Journal of Physical Chemistry Letters 13, 98–104 (2021).

29S. Appelt, F. W. Häising, U. Sieeling, A. Gordji-Nejad, S. Glöggler, and B. Blümich, “Paths from weak to strong coupling in NMR,” Physical Review A 81, 023420 (2010).

30J. W. Blanchard, M. P. Ledbetter, T. Theis, M. C. Butler, D. Budker, and A. Pines, “High-resolution zero-field NMR spectroscopy of aromatic compounds,” Journal of the American Chemical Society 135, 3607–3612 (2013).

31S. Alcicek, P. Put, V. Kontul, and S. Pustelnik, “Zero-field NMR j-spectroscopy of organophosphorus compounds,” The Journal of Physical Chemistry Letters 12, 787–792 (2021).

32T. F. Sjolander, M. C. D. Taylor, J. P. King, D. Budker, and A. Pines, “Transition-selective pulses in zero-field nuclear mag-
netic resonance,” Journal of Physical Chemistry A 120, 4343–4348 (2016).

33M. Jiang, J. Bian, X. Liu, H. Wang, Y. Ji, B. Zhang, X. Peng, and J. Du, “Numerical optimal control of spin systems at zero magnetic field,” Physical Review A 97 (2018), 10.1103/PhysRevA.97.062118.

34A. M. Thayer and A. Pines, “Composite pulses in zero-field NMR,” Journal of Magnetic Resonance (1969) 70, 518–522 (1986).

35C. J. Lee, D. Suter, and A. Pines, “Theory of multiple-pulse NMR at low and zero fields,” Journal of Magnetic Resonance (1969) 75, 110–124 (1987).

36J. Jeener, “Superoperators in magnetic resonance,” in Advances in Magnetic and Optical Resonance (Elsevier, 1982) pp. 1–51.

37(2022), Supplemental Material available at [URL inserted by publisher]. Contains: (i) Fourier coefficients of the BURP pulses; (ii) angle sets $\phi_1, \ldots, \phi_N$ for discrete BURP pulses; (iii) dac calibration.

38While the BURP pulse has a duration $\tau_p$, the pointwise approximation does not. This is because the actual rotation sequence does not depend on absolute value of $\tau_p$, as illustrated by Eq. (6).

39X. Yang, J. Lui, B. Gao, L. Lu, X. Wang, and B. C. Sanctuary, “Optimized phase-alternating composite pulse NMR,” Spectroscopy Letters 28, 1191–1201 (1995).

40A. Ramamoorthy, “Phase-alternated composite pulses for zero-field NMR spectroscopy of spin 1 systems,” Molecular Physics 93, 757–766 (1998).

41S. Husain, M. Kawamura, and J. A. Jones, “Further analysis of some symmetric and antisymmetric composite pulses for tackling pulse strength errors,” Journal of Magnetic Resonance 230, 145–154 (2013).

42M. C. D. Taylor, T. F. Sjolander, A. Pines, and D. Budker, “Nuclear magnetic resonance at millitesla fields using a zero-field spectrometer,” Journal of Magnetic Resonance 270, 35–39 (2016).

43J. Bian, M. Jiang, J. Cui, X. Liu, B. Chen, Y. Ji, B. Zhang, J. Blanchard, X. Peng, and J. Du, “Universal quantum control in zero-field nuclear magnetic resonance,” Physical Review A 95, 052342 (2017).

44M. C. D. Taylor and D. Sakellariou, “Low-cost, pseudo-Halbach dipole magnets for NMR,” Journal of Magnetic Resonance 277, 143–148 (2017).