Superadiabaticity in magnetic resonance

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Adiabaticity plays a central role in modern magnetic resonance experiments, as excitations with adiabatic Hamiltonians allow precise control of the dynamics of the spin states during the course of an experiment. Surprisingly, many commonly used adiabatic processes in magnetic resonance perform well even though the adiabatic approximation does not appear to hold throughout the process. Here we show that this discrepancy can now be explained through the use of Berry’s superadiabatic formalism, which provides a framework for including the finite duration of the process in the theoretical and numerical treatments. In this approach, a slow, but finite time-dependent Hamiltonian is iteratively transformed into time-dependent diagonal frames until the most accurate adiabatic approximation is obtained. In the case of magnetic resonance, the magnetization during an adiabatic process of finite duration is not locked to the effective Hamiltonian in the conventional adiabatic frame, but rather to an effective Hamiltonian in a superadiabatic frame. Only in the superadiabatic frame can the true validity of the adiabatic approximation be evaluated, as the inertial forces acting in this frame are the true cause for deviation from adiabaticity and loss of control during the process. Here we present a brief theoretical background of superadiabaticity and illustrate the concept in the context of magnetic resonance with commonly used shaped radio-frequency pulses. © 2008 American Institute of Physics. [DOI: 10.1063/1.3012356]

I. INTRODUCTION

Adiabaticity is a key concept in mechanics, in general, and quantum mechanics, in particular.1 Indeed, adiabatic processes play a central role in modern magnetic resonance experiments. Excitations with adiabatic Hamiltonians allow precise control of the dynamics of the spin states during the course of an experiment. This precise control is required in magnetic resonance imaging2 in order to guarantee the resolution and sensitivity which define the quality of an image and its reliability for medical diagnosis. Adiabatic excitations are also at the heart of experiments designed to record magnetic resonance signals outside the NMR magnet,3 with a view to developing portable imaging systems.4 Adiabatic control of spin dynamics is then of direct relevance to structural characterization in both solid5–7 materials and, for example, macromolecules in solution where adiabatic sweeps are used for broadband spin decoupling8,9 or dynamic polarization of the sample. Finally, adiabatic excitations will surely have potential for quantum computing applications when a large number of operations are performed.10

Although the basic idea behind an adiabatic process in magnetic resonance is deceptively simple, in practice, many different experimental designs have appeared over the years,8,11,12 with the aim of providing the best possible compromise between efficiency, broadbandedness, and a plethora of possible experimental imperfections such as offset,2,13,14 rf inhomogeneity,2,13,14 or even modulations due to sample rotation.5 In contrast, little development has been made in the theoretical description of adiabatic processes in magnetic resonance. In the following we present a rigorous theoretical approach for treating adiabatic processes in magnetic resonance. We show how this approach provides considerable insight into the mechanism of adiabatic spin dynamics and employ an iterative approach to introduce the notion of superadiabaticity for magnetic resonance. We believe that these theoretical advances will provide new insights into designing more efficient schemes for excitation in the future which will directly improve the quality of the various experiments discussed above.

A. Adiabaticity and superadiabaticity

A proper description of any quantum-mechanical system can be greatly simplified by choosing a suitable reference frame in which the corresponding Hamiltonian is in diagonal or block-diagonal form.1,15 Notably, the use of a propagator is more easily dealt with in a diagonal basis. Thus, the
Hamiltonian describing an adiabatic process can be represented in a time-dependent instantaneous diagonal frame,\textsuperscript{11,16,17} called the adiabatic basis. The effective Hamiltonian obtained in this basis generally consists of the sum of two contributions: the instantaneously diagonalized Hamiltonian, and the nonadiabatic coupling (the off-diagonal elements) which takes into account the finite rate at which the Hamiltonian changes. This coupling term can be neglected when the Hamiltonian is changing infinitely slowly, and the process is deemed perfectly adiabatic. This is never the case, in practice, and when analyzing and designing adiabatic processes, the finite rate of change must be included in the treatment.

In a series of papers in the 1980s, Berry\textsuperscript{18} provided such a framework. He showed that the Hamiltonian in the adiabatic frame can be retransformed (iteratively) into superadiabatic frames. This theoretical treatment has not so far been applied to magnetic resonance. Here, we show that the application of this framework explains troubling discrepancies in earlier theoretical descriptions of adiabatic processes in magnetic resonance. Specifically, we will show that the description of adiabatic process in the (time-dependent) adiabatic frame leads us to a new observation as follows. Usually, the adiabatic approximation requires the initial Hamiltonian to be aligned with the density operator describing the initial state, and also requires that the rate of change in the Hamiltonian must be much smaller than the Hamiltonian itself. This leads to the ideal type of magnetization inversion trajectory, familiar in magnetic resonance, shown in Fig. 1(a), and where the state of the system is always colinear with the Hamiltonian.

So far, improvements of adiabatic processes have focused on the fulfillment of these criteria. Accordingly, excitations with very low adiabaticity factors do not properly lock the magnetization, which, in turn, is not properly inverted at the end of the trajectory, as shown in Fig. 1(c). It is well known in NMR, however, that adiabatic processes with adiabaticity factors as low as 5 can still achieve perfect magnetization inversions.\textsuperscript{13} This should be somewhat surprising according to the usual adiabatic approximation, since this would require neglecting a coupling term representing 20% of the main interaction. Thus, although the magnetization is not locked to the effective field during these processes, as clearly shown in Fig. 1(b), the trajectory nevertheless proceeds smoothly to an exact inversion. In the following we show how the above behavior actually corresponds to the density operator being colinear with the effective Hamiltonian at all times in some adiabatic frame. This behavior is dubbed superadiabatic. We show here that superadiabatic behavior is indeed observed for many of the most commonly used adiabatic processes used in magnetic resonance, namely the hyperbolic secant\textsuperscript{13,19} and the tanh/tan\textsuperscript{12} pulse shapes. This superadiabatic picture explains why these pulse shapes work so well despite apparently low \( Q \) (adiabaticity) factors.

II. RESULTS AND DISCUSSION

A. Time-dependent rotating frames

Considering the evolution of a system under a Hamiltonian that is slowly varying with time, \( H_0(t) \), this Hamiltonian can be diagonalized at any instant according to

\[
D_1(t) = V_1^{-1}(t)H_0(t)V_1(t),
\]

where

\[
V_1(t) = V_1(t)e^{-i\Gamma(t)}
\]

and \([\Gamma(t),D_1(t)]=0\). In the initial frame the propagator \( U_0 \) for the system is then

\[
U_0(t) = T \exp \left[ -i\frac{\hbar}{T} \int_{-\infty}^{\infty} H_0(s) ds \right]
\]

\[
= V_1^{-1}(t)T e^{-i\phi} \int_{-\infty}^{\infty} [D_1(s)+C_1(s)] ds V_1^{-1}(\infty),
\]

with \( T \) being the time-ordering operator. Since the diagonalization is time dependent, the evolution will be governed by the sum of a diagonal term \( D_1 \) and a correction \( C_1 \) which appears to account for the "inertial fields" appearing in the moving frame:

\[
C_1(t) = -i\hat{\nabla}_1^{-1}(t)\nabla_1(t)
\]

\[
= -e^{i\phi} \int_{-\infty}^{\infty} [D_1(s)+C_1(s)] ds V_1^{-1}(\infty).
\]

In the traditional adiabatic approximation, the parts of \( C_1(t) \) orthogonal to \( D_1(t) \) are neglected (\(|C_1(t)| \gg D_1(t)\)) at all times), and only the parts of \( C_1(t) \) that commute with \( D_1(t) \) need then be retained. In the following, we further require that time-dependent eigenvectors \( |n_1(t)\rangle \) of \( H_0(t) \) undergo parallel transport by imposing

\[
\langle n_1(t)|n_1(t)\rangle = 0,
\]

and defining

\[
\Gamma_1(t) = \int |n_1(t)\rangle \langle n_1(t)| = \int [\nabla_1(t) V_1(t)]_{\text{diag}}.
\]

In this way, \( C_1(t) \) is always orthogonal to \( D_1(t) \), so in the adiabatic limit we look for representations \( V_1(t) \) in which the \( C_1(t) \) term can be completely neglected. The quality of this approximation is conveniently expressed by the so-called adiabaticity factor given by

\[
Q_1 = \min_{\rho \rightarrow \infty} \frac{|D_1(t)|}{|C_1(t)|}.
\]
B. Berry’s adiabatic iteration

In practice, no real process is infinitely slow enough to allow a proper adiabatic approximation. Thus, when analyzing and designing adiabatic processes, the finite duration (i.e., rate of change in the Hamiltonian) must be included in the theoretical and numerical treatments. Berry provided such a framework. Instead of applying the adiabatic approximation to Eq. (3), a better description can be achieved by considering the propagator in the frame defined by \( V_1 \) under the Hamiltonian \( H_1(t) = D_1(t) + C_1(t) \). Indeed \( H_1(t) \) can itself be instantaneously diagonalized into a second time-dependent diagonal frame (see Fig. 2). Since, by tradition, the frame defined by \( V_1 \) is dubbed the adiabatic frame, Berry dubbed this second frame superadiabatic. In the following, we will generally refer to the \( n \)th adiabatic frame.

In the superadiabatic frame, the instantaneous diagonal term is

\[
D_n(t) = V_n^{-1}(t)H_1(t)V_n(t),
\]

on which a new inertial field,

\[
C_n(t) = -i\dot{V}_n(t)V_n(t),
\]

acts as a perturbation. In this case, the relevant adiabaticity factor is the superadiabatic factor \( Q_2 \) defined as

\[
Q_2 = \min_{\|D_n(t)\|} \frac{\|D_n(t)\|}{\|C_n(t)\|}.
\]

If the second adiabatic frame is closer to the evolving Hamiltonian than in the first frame, \( Q_2 \) will be bigger than \( Q_1 \) and will be a more accurate description of the adiabaticity of the process.

The scheme can be applied iteratively (as sketched in Fig. 2), with the \( n \)th Hamiltonian given by

\[
H_n(t) = D_n(t) + C_n(t) = D_n(t) - i\dot{V}_n(t)V_n(t),
\]

where

\[
i\dot{V}_n(t)V_n(t) = ie^{iT_n(t)}i\dot{V}_n(t)V_n(t)e^{-iT_n(t)} - \dot{T}_n(t).
\]

Each transformation,

\[
V_n(t) = V_n(t)e^{-iT_n(t)},
\]

diagonalizes \( H_{n-1}(t) \) into \( D_n(t) \):

\[
D_n(t) = V_n^{-1}(t)H_{n-1}(t)V_n(t),
\]

thus moving into a frame where, in principle, the Hamiltonian clings even more closely to the evolving state. The \( n \)th time evolution propagator for the system in the \( n \)th instantaneous diagonal frame is

\[
U_n(t) = T \exp \left\{ -\left( i/\hbar \right) \int_0^t [D_n(s) + C_n(s)]ds \right\}.
\]

If the \( n \)th adiabaticity factor, given by

\[
Q_n = \min_{\|D_n(t)\|\|C_n(t)\|} \frac{\|D_n(t)\|}{\|C_n(t)\|},
\]

is sufficiently large, then in the \( n \)th frame, we make the adiabatic approximation by neglecting \( C_n(t) \). As before, one can show that the adiabatic approximation for the propagator in the \( n \)th instantaneous diagonal frame becomes

\[
U_n(t) = \exp \left\{ -\left( i/\hbar \right) \int_0^t D_n(s)ds \right\}.
\]

C. Phase and amplitude modulated pulses in magnetic resonance

Berry introduced this approach to show that no real process can ever be perfectly adiabatic (as will be discussed in Sec. II D). He used the example of a spin \( \frac{1}{2} \) moving on a cone (and using a different notation from that developed above). This approach has never been applied to problems in magnetic resonance, despite the extremely widespread applications of adiabatic spin rotations.

Adiabatic processes in magnetic resonance are typically implemented using a phase and amplitude modulated radio-frequency pulse to create an adiabatically changing Hamiltonian. As mentioned in Sec. I, if \( Q \) is very large, spin dynamics will be essentially adiabatic even if the process is not infinitely slow. For a \( Q \) factor around 1, however, the spin dynamics should not be adiabatic. Here we use the superadiabatic iteration process to analyze some commonly used adiabatic inversion pulse shapes and show how their inversion efficiencies can only be understood using optimal superadiabatic frames. This analysis notably provides us with a rigorous definition of adiabaticity for magnetic resonance.

In the following discussion, we restrict ourselves to the case where the Hamiltonian is defined by an isotropic shift, \( \Omega \), (e.g., a single spin in solution) and a rf excitation of duration \([0, \tau]\) in the transverse plane. In the rotating frame, \((x, y, z)\), the Hamiltonian is given by
\[ H(t) = \Omega(t) + \omega(t) \mathbf{I}_x \cos \varphi(t) + \mathbf{I}_y \sin \varphi(t), \]  

where \( \omega(t) \) and \( \varphi(t) \) describe the time-dependent amplitude and phase of the excitation, as illustrated in Figs. 3(a) and 3(f) for the case of a tanh/tan shape pulse.\(^{12}\) Transforming this into a modulated frame \((x_0, y_0, z_0)\) rotating about \( z \) to remove the time dependence of \( \varphi(t) \)\(^{13}\) gives

\[ H_0(t) = \Delta \Omega(t) \mathbf{I}_{x_0} + \omega(t) \mathbf{I}_{y_0}, \]  

where \( \Delta \Omega(t) \) is the instantaneous carrier frequency offset, given by

\[ \Delta \Omega(t) = \Delta \omega(t) - \Omega, \]  

where \( \Delta \omega(t) = d \varphi(t)/dt \). This is sketched in Fig. 3(b). The iterative transformations into different adiabatic frames provide a stronger insight into the behavior of the system. To begin with, we place ourselves in a frame which follows the Hamiltonian. This first \((n=1)\) adiabatic frame \((x_1, y_1, z_1)\) [see Fig. 3(c)] is tilted by an angle \( \alpha_0(t) \) with respect to the modulated frame, given by

\[ \alpha_0(t) = \arctan \left( \frac{\Delta \omega(t)}{\omega(t)} \right), \]  

and illustrated in Fig. 3(g) for the tanh/tan shape pulse. The orthogonal matrix that achieves this transformation is a simple rotation around the \( y_0 \) axis and as a consequence \( \Gamma_1(t) \) will be zero and one obtains

\[ V_1(t) = V(t) = e^{-i \alpha_0(t)} I_{y_0}. \]  

In this frame, the Hamiltonian is instantaneously diagonal:
\[
D_1(t) = V_1(t)H_0(t)V_1(t) = \Omega_1(t)I_{z_1},
\]

(23)

with
\[
\Omega_1(t) = \sqrt{\omega_0^2(t) + \Delta \omega^2(t)},
\]

(24)

and is subject to a perturbation \( C_1(t) \), given by
\[
C_1(t) = -\frac{d\alpha_0(t)}{dt}I_{y_1}.
\]

(25)

At this stage, we rediscover the conventional adiabaticity criterion which requires that
\[
\|D_1(t)\| \gg \|C_1(t)\| \quad \text{or} \quad \Omega_1(t) \gg \left|\frac{d\alpha_0(t)}{dt}\right|,
\]

(26)

with
\[
Q_1 = \min_{\alpha_0(t) = 0, \pi} \frac{\Omega_1(t)}{|d\alpha_0(t)/dt|} \gg 1,
\]

(27)

such that \( C_1(t) \) would be truncated by \( D_1(t) \) at all times during the excitation. If this criterion is fulfilled, \( C_1(t) \) can be neglected and the Hamiltonian is coincident with \( D_1(t) \) over the whole pulse. Hence, magnetization can be locked in this frame by such a Hamiltonian. If not, the resulting Hamiltonian
\[
H_1(t) = D_1(t) + C_1(t)
\]

(28)

in the first adiabatic frame is in fact tilted from the \( z_1 \) axis by an angle \( \alpha_1(t) \) [see Fig. 3(c)] which is
\[
\alpha_1(t) = \arctan \frac{\|C_1(t)\|}{\|D_1(t)\|},
\]

(29)

that is
\[
Q_1 = \min_{\alpha_0(t) = 0, \pi} \frac{1}{\tan \alpha_1(t)}.
\]

(30)

The interest of this clearly emerges when comparing two different tanh/tanh shape pulses applied with the same \( \omega_0 \) but with different pulse durations (2 ms versus 100 \( \mu s \)). Both pulses invert magnetization almost equally well on resonance, even though the \( Q_1 \) factor for the 2 ms pulse is much larger than 1 (\( Q_1 = 95 \)) as can be deduced from the dashed curve plotting \( \alpha_1(t) \) in Fig. 3(h)] whereas the short pulse has \( Q_1 \approx 6 \). Thus, one would not expect inversion with the shorter pulse to be as good as with the longer pulse. However this is not consistent with experiment. For this latter excitation, the above procedure can then be applied iteratively with the hope of more accurately following the Hamiltonian. Defining
\[
V_2(t) = e^{i\alpha_1(t)}I_{z_1},
\]

(31)

we transform the adiabatic frame \((x_1, y_1, z_1)\) into the superadiabatic frame \((x_2, y_2, z_2)\), where
\[
D_2(t) = \Omega_2(t)I_{z_2}, \quad \text{and} \quad C_2(t) = \frac{d\alpha_0(t)}{dt}I_{z_2},
\]

(32)

with
\[
\Omega_2(t) = \sqrt{\Omega_1^2(t) + \alpha_0^2(t)},
\]

(33)

as illustrated in Fig. 3(d). Most interestingly, Fig. 3(i) shows that the new diagonal term \( D_2(t) \) is subject to a relatively weaker perturbation \( C_2(t) \), such that the angle \( \alpha_2(t) = \arctan(\|C_2(t)\|/\|D_2(t)\|) \gg (\|C_2(t)\|/\|D_2(t)\|) \) has a smaller excursion during the whole excitation. In this case, the minimum value of \( Q_2 \approx 100 \) and the pulse fulfills criteria for adiabaticity thereby explaining the excellent inversion behavior observed. Even better representations, where the evolving Hamiltonian may appear even more static, could be obtained with additional iteration, using transformations
\[
V_n(t) = \exp\left\{-i\alpha_{n-1}(t)e^{d(n-1)/2\Omega_{n-1}}I_{y_{n-1}}e^{-i(n-1)/2\Omega_{n-1}}\right\},
\]

(34)

which progressively moves the \((n-1)\)th adiabatic frame \((x_{n-1}, y_{n-1}, z_{n-1})\) into the \(n\)th adiabatic frame \((x_n, y_n, z_n)\) where the diagonal Hamiltonian is
\[
D_n(t) = \Omega_n(t)I_{z_n},
\]

(35)

with
\[
\Omega_n(t) = \sqrt{\Omega_{n-1}(t) + \alpha_{n-2}^2(t)}.
\]

(36)

and where the perturbation will be
\[
C_n(t) = -\alpha_{n-1}(t)e^{d(n-1)/2\Omega_{n-1}}I_{y_{n-1}}e^{-i(n-1)/2\Omega_{n-1}}.
\]

(37)

This is illustrated for the third adiabatic frame in Figs. 3(e) and 3(j), with \( Q_2 \) values of 176 and 1.3 \( \times 10^6 \). These extremely high \( Q \) values in the superadiabatic frame explain why certain adiabatic pulses with low \( Q \) values in the adiabatic \((k=1)\) frame still produce essentially perfect inversion in magnetic resonance.

### D. Divergence of the superadiabatic iterations

While each iteration can bring us into a frame where the evolving Hamiltonian will appear to move closer and closer around the north pole, eventually continued iterations, as Berry showed, must bring us into frames where the evolving Hamiltonian spirals further and further away from the pole. This must be true because any finite duration process will always have nonadiabatic effects (transitions), and these cannot be escaped simply through iterative frame transformations.

This eventual divergence in the \(n\)th frame can be understood by close examination of the \( \Omega_n(t) \) and \( \alpha_n(t) \). If \( |\alpha_n(t)| \ll |\Omega_n(t)| \), then at each iteration \( \Omega_n(t) = \Omega_1(t) \) and the profile of the excursion \( \alpha_n(t) \) of the effective field in the \(n\)th adiabatic frame satisfies the iterative differential equation
\[
\frac{\alpha_n(t)}{\Omega_n(t)} = \frac{\frac{d^2\alpha_n(t)}{dt^2}}{\frac{d\alpha_n(t)}{dt}} = \frac{1}{\alpha_0^2(t)} \frac{d^2\alpha_0(t)}{dt^2},
\]

(38)

independently from the details of the specific excitation under consideration (i.e., independently of the amplitude and phase modulation profile employed). From Eqs. (37) and (38), one can expect the \( C_n \) to become smaller with initial iterations due to the \( 1/\omega_0^2 \) dependence, as seen in Fig. 3. Eventually, however, the number of derivatives of \( \alpha_0 \) re-
required to calculate \( \alpha_n \) at higher iterations will cause the \( \alpha_n \) to grow beyond \( \Omega_n \) in magnitude. As detailed in Appendix B, the maximal amplitude of \( \alpha_n \) will vary according to

\[
\max_{n=1-\tau_p} |\alpha_n| \approx \frac{n!}{(\omega_1 \tau_p)^n}.
\]

The initial decrease from the \((\omega_1 \tau_p)^n\) is ultimately overwhelmed by the increase from \(n!\). Thus, the optimum superadiabatic frame is \( n = \Omega_1 \tau_p \), where the smallest maximal amplitude is

\[
\alpha_{\omega_1 \tau_p} = \Delta \omega \sqrt{2 \pi \omega_1 \tau_p e^{-\omega_1 \tau_p}}.
\]

E. Criteria for magnetization inversion: Superadiabatic Q factors

The divergence of the iterated change in frame appears clearly in Fig. 4, where the first ten \( Q_n \) factors are plotted for two tanh/tan excitations. The ordinary \( Q_1 \) factors of 6.6 and 2.6, respectively, would suggest that neither of these two processes is adiabatic. Nonetheless, the 100 \( \mu \)s pulse inverts magnetization on resonance with an efficiency of more than 99%, while the second has an inversion efficiency of less than 95%

In Fig. 4, for both excitations, the \( Q_n \) grow to a maximum at \( n = 6 \) and 4, respectively, and then decrease as expected from the considerations of divergence. For the 100 \( \mu \)s excitation, however, the \( Q_n \) factors are greater than 100 as soon as \( n > 2 \) with a maximum for \( Q_6 \) of roughly 1500. This means that the perturbation \( C_n(t) \) varies slowly (adiabatically), and that the static spin can thus be locked along the effective field \( \Omega_n(t)I_{z_n} \) in an adiabatic frame. On the contrary, in the case of the short excitation, magnetization is never locked sufficiently well to the field, since in all the frames the perturbation \( C_n(t) \) is not negligible and the adiabatic condition is thus never achieved. By defining a superadiabatic \( Q \) factor as

\[
\frac{1}{Q} = \min_{n} \frac{1}{Q_n} = \min_{n} \left[ \max_{n \in [0, T]} \left( \frac{||C_n(t)||}{||D_n(t)||} \right) \right],
\]

we can restate a criterion for good magnetic resonance adiabatic processes as follows: perfect magnetization inversion can be achieved whenever the magnetization is locked in ANY of the superadiabatic frames, i.e., if \( 1/Q \) is negligible. As explained in Sec. II D, the optimum frame occurs when \( n = \max \omega_1 \tau_p \). With this definition we now find that the efficiency of inversion is better characterized by the value of the \( Q \) factor than by the traditional \( Q \) factor, which does not take the appropriate locking process in effect. For example, both a 100 \( \mu \)s hyperbolic secant shape pulse with 200 kHz sweep and 40 kHz rf power and a tanh/tan shape pulse of 40 \( \mu \)s with a sweep of 2 MHz and 40 kHz rf power have identical \( Q \) factors of 2, even though their inversion efficiencies are 90% and 95%, respectively. This difference in inversion efficiencies is easily explained once one realizes that their superadiabatic \( Q \) factors are 6.3 and 8.7, respectively.

F. Superadiabatic magnetization trajectories

The considerations of Secs. II A through II E now allow us to fully understand the inversion efficiencies in Fig. 1. The approach also provides a tool for accurately describing the magnetization trajectories and notably the anomalous trajectory in Fig. 1(b).

In the case of a perfectly adiabatic process, the magnetization is aligned with the Hamiltonian \( H_0 \) at the beginning, stays locked during the whole excitation, and is static in the \( n = 1 \) adiabatic frame. The trajectory in the modulated frame can then be explicitly evaluated with an initial state in the modulated frame \( \phi_0(0) = \ket{z_0, +} \) the trajectory is given by

\[
\psi(t) = V_1(t) \phi_0(t) = \exp(i\alpha_0 L_j) \phi_0(t),
\]

\[
= \cos \frac{\alpha_0}{2} \ket{z_0, +} + \sin \frac{\alpha_0}{2} \ket{z_0, -}.
\]

The magnetization thus travels from the \( +z_0 \) to the \( -z_0 \) axis with a perfectly circular trajectory in the \( x_0 = z_0 \) plane [Fig. 5(a)]. On the contrary, the magnetization will not appear as static anymore in the \( n = 1 \) frame in the case of a superadiabatic process. If locking is achieved in the \( n = 2 \) adiabatic frame, the magnetization will feature an excursion in the \( y_1 z_1 \) plane when viewed the \( n = 1 \) frame. When transformed back into the initial modulated frame, this excursion will appear as a deviation from the circular trajectory [Figs. 5(b) and 1(b)]:

\[
\phi_0(t) = V_1(t) V_2(t) \phi_0(t) = \exp(i\alpha_0 L_j) (-i\alpha_0 L_j) \phi_0(t).
\]

However, one should note that, as with all adiabatic processes, if the initial state is not aligned with the Hamiltonian in the most relevant (adiabatic or superadiabatic) frame, then the magnetization will precess around the field and will not necessarily follow the Hamiltonian.

More generally, if the magnetization starts aligned with the Hamiltonian \( H_0 \) in any \( n \)th frame and remains locked during the process (according to the superadiabaticity criterion defined above), the trajectories in any upstream frame \( k < n \) can be calculated explicitly as
\[ |\psi(t)\rangle = \prod_{i=k}^{n} V^i(t)|\psi(0)\rangle. \]  \[ (44) \]

Clearly, the complexity of the resulting trajectory grows with the number of frame changes needed to reach a superadiabatic condition [Figs. 5(c) and 5(d)].

**G. Conclusion**

We have explained through the introduction of the notion of superadiabaticity why adiabatic processes in magnetic resonance often work when the conventional criteria for adiabaticity says they will not. Specifically, we have shown, using time-dependent diagonal frames, how to derive analytical expressions for the effective Hamiltonians and the spin system propagator during an adiabatic process. The model is applied to adiabatic rf sweeps commonly used in NMR experiments. The spin system evolution during these adiabatic processes shows that the adiabatic approximation cannot be rigorously made for commonly used adiabaticity factors, and yet, these excitations manage to invert the magnetization. In fact, we show here that the magnetization is effectively locked, not by the effective field in the conventional modulated frame, but rather by the effective field in an adiabatic representation. A new superadiabaticity factor is introduced and shown to provide a more relevant characterization of these adiabatic magnetic resonance excitation schemes. Such a concept opens the possibility for new routes for the optimization of adiabatic process in magnetic resonance, and following trajectories in the superadiabatic frames may shed light in designing new processes in areas as diverse as magnetic resonance imaging, where it could lead to improved image contrast, quantum computing, where it could lead to better control of quantum coherences, and to structural characterization where it will lead to more accurate dis-
tance determinations in NMR studies in liquid and solid-state, in proteins or inorganic materials. This method could be extended to more complicated Hamiltonians, and it has the capability to provide analytical expressions in magnetic resonance for coupled spin systems as well as for nuclei with spin $I > \frac{1}{2}$.

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APPENDIX A: BERRY’S EXAMPLE

Here, we reformulate the example given in Berry’s\textsuperscript{18} original treatment according to the formalism developed in the main text.

1. Adiabatic limit

Consider the case of a spin $\frac{1}{2}$ system where the Hamiltonian makes one sweep around on a cone of opening angle $\vartheta$ with a variable azimuth $\alpha(t)$ [Fig. 6(a)] according to

$$H_0(t)/\hbar = \omega_1 [I_z \cos \vartheta + [I_x \cos \alpha(t) + I_y \sin \alpha(t)] \sin \vartheta]$$

$$= \omega_1 e^{-i\alpha(t)} I_z e^{-i\vartheta I_0},$$

$$= \omega_1 e^{-i\alpha(t)} I_z e^{-i\vartheta I_0} e^{i\alpha(t)} I_z,$$

and we have $H_0(-\infty) = H_0(+\infty)$, that is $\alpha(-\infty) = 0$ and $\alpha(+\infty) = 2\pi$.

This Hamiltonian can be transformed into the instantaneous diagonal frame [Fig. 6(b)], $(x_0, y_0, z_0)$, starting first with a rotation about the $z_0$ axis in the stationary frame $(x_0, y_0, z_0)$ by an angle $\alpha(t)$ followed by a rotation about the $y'$ axis in the rotating frame, $(x', y', z')$, by an angle $\vartheta$. Note that $z_0 = z'$ and $y' = y_1$. Thus, applying the transformation

$$V_1(t) = e^{-i\alpha(t)} I_z e^{-i\vartheta I_0},$$

to $H_0(t)$ yields

$$D_1 = V_1(t) H_0(t) V_1(t) = \omega_1 I_z.$$

The condition

$$\langle n_1(t) | \tilde{n}_1(t) \rangle = 0,$$

leads to

$$\langle n_1(t) | \tilde{V}_1(t) V_1(t) | n_1(t) \rangle = 0.$$

Thus, we enforce parallel transport of the time-dependent eigenvectors by defining:

$$\tilde{\Gamma}_1(t) = \sum_n \langle n(t)| \tilde{n}_1(t) \rangle | n(t) \rangle$$

Since

$$i \tilde{V}_1(t) V_1(t) = \tilde{\alpha}(t)[I_z \cos \vartheta + I_y \sin \vartheta],$$

we define

$$\tilde{\Gamma}_1(t) = \tilde{\alpha}(t) I_z \cos \vartheta.$$

The adiabatic approximation propagator requires that $|| C_{\tilde{\alpha}(t)} || \ll || D_1 ||$, that is, $| \tilde{\alpha}(t) \sin \vartheta | \ll \omega_1$. If this is the case, in the instantaneous diagonal frame the propagator becomes

$$U_1(t) = e^{i\tilde{\Gamma}_1(t)} I_z e^{i\vartheta I_0} e^{-i\alpha(t)} I_z.$$

The initial state function in the initial instantaneous diagonal frame is an eigenstate of the initial Hamiltonian:

$$| \psi_1(-\infty) \rangle = | z_1, + \rangle,$$

that is,

$$| \psi_0(-\infty) \rangle = | z_1, + \rangle = V_1(-\infty) | \psi_1(-\infty) \rangle = \cos \frac{\vartheta}{2} | z_0, + \rangle + \sin \frac{\vartheta}{2} | z_0, - \rangle.$$

In the limit $| \tilde{\alpha}(t) \sin \vartheta | \ll \omega_1$, in the instantaneous diagonal frame, the state evolves adiabatically according to

FIG. 6. (Color) Hamiltonian sweeping around a cone of opening $\vartheta$ with variable azimuth $\alpha(t)$ viewed from the laboratory frame (a) and from the frame in which the Hamiltonian is instantaneously diagonal (adiabatic frame) (b).
\[ |\psi_1(t)\rangle = U_1(t)|\psi_1(-\infty)\rangle = e^{-i\left(\omega_1 t + \cos \theta \int_{-\infty}^{t} \dot{\alpha}(s) ds\right)} |z_{1,1}^+,+\rangle. \]  
(A12)

After a full rotation of the Hamiltonian, where \( \int_{-\infty}^{t} \alpha(s) ds \rightarrow 2\pi \), the system will end up to its starting position, but acquires a phase which comprises a dynamical contribution as well as a geometric one:

\[ |\psi_1(t)\rangle = e^{-i(\omega_1 t + 2\pi \cos \theta)/2} |z_{1,1}^+,+\rangle. \]  
(A13)

The geometric contribution to this phase \(^{21}\) can be evaluated by comparing the system to the initial state of an unevolved (static) Hamiltonian, which acquires only a dynamical phase:

\[ |\varphi_1(t)\rangle = e^{-i\omega_1 t/2} |z_{1,1}^+,+\rangle, \]  
(A14)

so the phase difference acquired during the \( 2\pi \) rotation of the field is

\[ \gamma_1 = -\pi(1 - \cos \theta). \]  
(A15)

2. Iterative approach

Now we reformulate the example of the magnetic field sweeping around a cone using the iterative approach developed in Sec. II B. Without the adiabatic approximation, the full Hamiltonian in the adiabatic frame,

\[ H_1(t) = \omega_1 I_{z_1} + e^{i\alpha(t) \cos \theta I_{1,1} \sin \theta} e^{-i\alpha(t) \cos \theta I_{1,1}}. \]  
(A16)

The Hamiltonian can be transformed into a new instantaneous diagonal frame, \((x_2, y_2, z_2)\), using the unitary transformation

\[ V_2(t) = e^{i\alpha(t) \cos \theta I_{1,1} \sin \theta} e^{i\alpha_2 I_{2,2}}, \]  
(A17)

where

\[ \alpha_2(t) = \arctan \left( \frac{\dot{\alpha}(t) \sin \theta}{\omega_1} \right), \]  
(A18)

to obtain

\[ D_2(t) = V_2^\dag(t) H_1(t) V_2(t) = \omega_2 I_{z_2}, \]  
(A19)

where

\[ \omega_2 = \sqrt{\omega_1^2 + (\dot{\alpha}(t) \sin \theta)^2}, \]  
(A20)

and

\[ iV_2^\dag(t) V_2(t) = \dot{\alpha}(t) I_{x_2} \cos \theta \sin \alpha_2(t) - i \dot{\alpha}_2(t) I_{y_2} \cos \theta \cos \alpha_2(t). \]  
(A21)

Thus, we define

\[ \Gamma_2(t) = \dot{\alpha}(t) I_{x_2} \cos \theta \cos \alpha_2(t), \]  
(A22)

and make the adiabatic approximation to obtain propagator in the \( n=2 \) instantaneous diagonal frame

\[ U_2(t) = \exp \left\{ i \Gamma_2(t) \cos \theta \int_{-\infty}^{t} \dot{\alpha}(s) \cos \alpha_2(s) ds \right\} \times \exp \left\{ -i \int_{-\infty}^{t} \omega_2(s) I_{z_2} ds \right\}. \]  
(A23)

The initial state of the system \(|\psi_2(-\infty)\rangle\) is an eigenstate of the Hamiltonian \( D_2(-\infty) \), but it is also an eigenstate of \( \Gamma_1(-\infty) \):

\[ |\psi_2(-\infty)\rangle = |z_{2,2}^+,+\rangle. \]  
(A24)

At any time, in the instantaneous diagonal frame, in the adiabatic limit of \( \dot{\alpha}(t) \sin \theta \sin \alpha_2(t) / \omega_2 \rightarrow 0 \), the state of the system is

\[ |\psi_2(t)\rangle = U_2(t)|\psi_2(-\infty)\rangle. \]  
(A25)

Thus, after one complete rotation (at \( t \rightarrow \infty \), where \( \alpha(t) \rightarrow 2\pi \), the accumulated phase is

\[ \gamma_2^{\text{tot}} = \frac{1}{2} \left\{ \cos \alpha \int_{-\infty}^{t} \dot{\phi}(s) \cos \beta(s) ds \right\} + \frac{1}{2} \left\{ - \int_{-\infty}^{t} \omega_2(s) ds \right\}. \]  
(A26)

As in Berry,\(^{18}\) we explicit the consequences of the limit \( \dot{\alpha}(t) \sin \theta \sin \alpha_2(t) / \omega_2 \rightarrow 0 \) by expanding the result in series of \( \alpha(t) \):

\[ \dot{\alpha}(t) \sin \theta \sin \alpha_2(t) / \omega_2 = \frac{\dot{\alpha}(s) \cos \theta \omega_2}{\omega_2} = \frac{\dot{\alpha}(s) \cos \theta}{\omega} - \frac{\cos \theta \sin^2 \theta}{2 \omega_1^2} \alpha^3 \]  
(A27)

and

\[ \omega_2 = \omega_1 + \frac{\sin^2 \theta \dot{\alpha}^2}{2 \omega_1}, \]  
(A28)

so that

\[ \gamma_2^{\text{tot}} = \pi + 1/2 \int_{-\infty}^{t} \dot{\alpha}(s) \cos \theta - 1/2 \int_{-\infty}^{t} \cos \theta \sin^2 \theta \alpha^3 - \frac{1}{2} \int_{-\infty}^{t} \omega_1 - 1/2 \int_{-\infty}^{\infty} \frac{\sin^2 \theta \dot{\alpha}^2}{2 \omega_1} \]  
(A29)

\[ = - \left[ \pi(1 - \cos \theta) + \int_{-\infty}^{t} \omega_2 ds + \frac{\sin^2 \theta}{4 \omega_1} \int_{-\infty}^{t} \alpha^3(s) ds \right]. \]  
(A30)

An eigenstate of a static magnetic field (waiting in the same position as it was at \( -\infty \)) would have acquired only a phase:

\[ \gamma_{\text{ref}} = \int_{-\infty}^{\infty} \omega_2 ds, \]  
(A30)

so the phase difference acquired during the \( 2\pi \) rotation of the field is
FIG. 7. (Color) Maclaurin’s sinusoidal spirals and universal $Q_n$ factors for various $n$.

\[ f_n(t) = \left(1 + \frac{r^2}{\omega_1^2 \tau_p^2}\right)^{-1/2(n+1)} \times \sin \left[\frac{1}{2} n \pi + (n+1)\arctan\left(\frac{r}{\omega_1 \tau_p}\right)\right]. \] (B2)

This limit holds independently from the details of the specific excitation under consideration (i.e., independently from the shape of the amplitude and phase modulation profile employed). The solutions of Eq. (B2) describe a family of curves, which are the projections of Maclaurin’s sinusoidal spirals (the “universal loops” described by Berry), some of which are described in Fig. 7.

1. A. Messiah, Quantum Mechanics (North-Holland, Amsterdam, 1965).