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Rotation Operator Propagators for Time-varying Radiofrequency Pulses in NMR Spectroscopy: Applications to Shaped Pulses and Pulse Trains

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Abstract

The propagator for trains of radiofrequency pulses can be directly integrated numerically or approximated by average Hamiltonian approaches. The former provides high accuracy and the latter, in favorable cases, convenient analytical formula. The Euler-angle rotation operator factorization of the propagator provides insights into performance that are not as easily discerned from either of these conventional techniques. This approach is useful in determining whether a shaped pulse can be represented over some bandwidth by a sequence $\tau_1 - \mathbf{R}_\varphi(\beta) - \tau_2$, in which $\mathbf{R}_\varphi(\beta)$ is a rotation by an angle β around an axis with phase φ in the transverse plane and τ_1 and τ_2 are time delays, allowing phase evolution during the pulse to be compensated by adjusting time periods prior or subsequent to the pulse. Perturbation theory establishes explicit formulas for τ_1 and τ_2 as proportional to the average transverse magnetization generated during the shaped pulse. The Euler-angle representation of the propagator also is useful in iterative reduction of pulse-interrupted-free precession schemes. Application to Carr-Purcell-Meiboom-Gill sequences identifies an eight-pulse phase-alternating scheme that generates a propagator nearly equal to the identity operator.

Keywords

Rotation operator; Euler angle; Perturbation expansion; Shaped pulse; CPMG

1. Introduction

Numerous techniques in NMR spectroscopy utilize radiofrequency (rf) pulses in which the carrier frequency, amplitude, and/or phase are time-dependent. Examples include shaped

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pulses, shifted laminar pulses, adiabatic pulses, and pulse-interrupted-free-precession sequences [1]. For an isolated spin, in the absence of scalar couplings and ignoring relaxation, evolution of the density operator during such a pulse scheme is described by

$$\sigma(t) = \mathbf{U} \sigma(0) \mathbf{U}^{-1} \quad (1)$$

in which $\sigma(t)$ is the density operator, t is the length of the pulse, and $\mathbf{U}$ is the propagator given by

$$\mathbf{U} = \mathbf{T} \exp \left[-i \int_0^t \left\{ \omega_x(t') I_x + \omega_y(t') I_y + \Omega(t') I_z \right\} dt' \right] \quad (2)$$

$\mathbf{T}$ is the Dyson time-ordering operator, $\omega_x(t)$ and $\omega_y(t)$ are the time-dependent rf amplitudes with x - and y -phase, respectively, and $\Omega(t)$ is the time-dependent resonance offset of the nuclear spin under consideration. The two most common approaches for calculating the evolution of the density operator under the propagator are average Hamiltonian theory (AHT) [2, 3], which has the advantage of yielding analytically tractable results in many instances, and direct numerical integration, which has the advantage of high accuracy. In the latter case, the integral is expressed as a summation using a time step Δt sufficiently short that the exponential of the sum can be expressed as the product of individual rotations during each time step [1].

The rotation operator formalism of Sanctuary and coworkers [4] and Siminovich [5, 6] provides an alternative approach and is the subject of the present work. In this method, the propagator given in Eq. (2) is expressed as:

$$\mathbf{U} = \exp[-i\gamma(t)I_z] \exp[-i\beta(t)I_x] \exp[-i\alpha(t)I_z] \quad (3)$$

Thus, evolution of the density operator is calculated as the product of three individual rotation operations by the Euler angles $\alpha(t)$, $\beta(t)$, and $\gamma(t)$. As this approach makes clear, any time-varying rf pulse train can be represented as an x -rotation flanked by two (not necessarily identical) z -rotations. The initial z -rotation is inconsequential for an excitation pulse applied to equilibrium z -magnetization, so that any excitation pulse is described by an x -rotation followed by a z -rotation. Inversion of the initial equilibrium density operator is described simply by $\cos[\beta(t)]$. The present work employs the rotation operator formalism to characterize shaped and other time-dependent rf pulse schemes commonly employed in modern NMR spectroscopy of biological macromolecules.

The off-resonance effects of a square 90° pulse are known to be approximated by a sequence $\tau - 90^\circ_x - \tau$, in which $\tau = 2 \tau_p / \pi$ and τ_p is the on-resonance pulse length [1, 7]. Recent work has used numerical methods to approximate the off-resonance effects of shaped pulses by a pulse rotation preceded and/or followed by a time delay [8]. As Eq. 3 indicates, such relationships arise whenever $\alpha(t)$ and/or $\gamma(t)$ are proportional to the resonance offset of spins

within the bandwidth of the shaped pulse and such dependence can be required as part of the optimization of shaped pulses [9].

2. Theory

The functions $\alpha(t)$, $\beta(t)$, and $\gamma(t)$ are found by differentiating Eqs. (2) and (3) with respect to time. The derivative of Eq. (2) is simply:

$$\frac{d\mathbf{U}}{dt} = -i \{ \omega_x(t) I_x + \omega_y(t) I_y + \Omega(t) I_z \} \mathbf{U} \quad (4)$$

The derivative of Eq. (3) is

$$\begin{aligned} \frac{d\mathbf{U}}{dt} = & -i \left\{ \frac{d\gamma(t)}{dt} I_z \right. \\ & + \frac{d\beta(t)}{dt} \exp[-i\gamma(t) I_z] I_x \exp[-i\beta(t) I_x] \exp[-i\alpha(t) I_z] \\ & + \frac{d\alpha(t)}{dt} \exp[-i\gamma(t) I_z] \exp[-i\beta(t) I_x] I_z \exp[-i\alpha(t) I_z] \left. \right\} \mathbf{U} \quad (5) \\ = & -i \left\{ \frac{d\gamma(t)}{dt} I_z + \frac{d\beta(t)}{dt} (I_x \cos[\gamma(t)] + I_y \sin[\gamma(t)]) \right. \\ & + \frac{d\alpha(t)}{dt} (I_z \cos[\beta(t)] - I_y \sin[\beta(t)] \cos[\gamma(t)] + I_x \sin[\beta(t)] \sin[\gamma(t)]) \left. \right\} \mathbf{U} \end{aligned}$$

Equating the terms in Eqs. (4) and (5) that are proportional to the same operator I_x , I_y , or I_z yields a system of equations:

$$\begin{aligned} \omega_x(t) &= \frac{d\beta(t)}{dt} \cos[\gamma(t)] + \frac{d\alpha(t)}{dt} \sin[\beta(t)] \sin[\gamma(t)] \\ \omega_y(t) &= \frac{d\beta(t)}{dt} \sin[\gamma(t)] - \frac{d\alpha(t)}{dt} \sin[\beta(t)] \cos[\gamma(t)] \\ \Omega(t) &= \frac{d\gamma(t)}{dt} + \frac{d\alpha(t)}{dt} \cos[\beta(t)] \end{aligned} \quad (6)$$

These equations can be rearranged to give:

$$\frac{d\alpha(t)}{dt} = \{ \omega_x(t) \sin[\gamma(t)] - \omega_y(t) \cos[\gamma(t)] \} / \sin[\beta(t)] \quad (7a)$$

$$\frac{d\beta(t)}{dt} = \omega_x(t) \cos[\gamma(t)] + \omega_y(t) \sin[\gamma(t)] \quad (7b)$$

$$\frac{d\gamma(t)}{dt} = \Omega(t) - \{ \omega_x(t) \sin[\gamma(t)] - \omega_y(t) \cos[\gamma(t)] \} / \tan[\beta(t)] \quad (7c)$$

Equations (7b) and (7c) are a pair of coupled differential equations for $\beta(t)$ and $\gamma(t)$.

As first demonstrated by Zhou *et al.* [4] in the context of NMR, defining:

$$f(t) = \tan \left[\frac{\beta(t)}{2} \right] \exp[i\gamma(t)] \quad (8)$$

enables Eqs. (7b) and (7c) to be combined to give the Riccati equation:

$$\begin{aligned}\frac{df(t)}{dt} &= \frac{1}{2} [\omega_x(t) - i\omega_y(t)] f^2(t) + i\Omega(t)f(t) + \frac{1}{2} [\omega_x(t) + i\omega_y(t)] \\ &= \frac{1}{2}\omega^-(t)f^2(t) + i\Omega(t)f(t) + \frac{1}{2}\omega^+(t)\end{aligned}\quad (9)$$

where $\omega^\pm(t) = \omega_x(t) \pm i\omega_y(t)$. From the definition in Eq. (8),

$$\begin{aligned}\beta(t) &= \cos^{-1} \left[\frac{1 - |f(t)|^2}{1 + |f(t)|^2} \right] \\ \gamma(t) &= \text{Arg}[f(t)]\end{aligned}\quad (10)$$

and by construction, $\alpha(0) = -\gamma(0)$, $\beta(0) = 0$, and $f(0) = 0$.

The Riccati equation also can be converted to a second-order linear homogeneous equation by making the substitution:

$$\frac{d \ln y(t)}{dt} = -\frac{1}{2}\omega^-(t)f(t) \quad (11)$$

to yield:

$$\frac{d^2 y(t)}{dt^2} - \left[\frac{d \ln \omega^-(t)}{dt} + i\Omega(t) \right] \frac{dy(t)}{dt} + \frac{1}{4} |\omega(t)|^2 y = 0 \quad (12)$$

If $\omega^-(t)$ is written as $|\omega(t)|\exp[-i\phi(t)]$, then:

$$\frac{d^2 y(t)}{dt^2} - \left[\frac{d \ln |\omega(t)|}{dt} + i \left\{ \Omega(t) - \frac{d\phi(t)}{dt} \right\} \right] \frac{dy(t)}{dt} + \frac{1}{4} |\omega(t)|^2 y = 0 \quad (13)$$

and the term in curly braces can be regarded as a time-dependent resonance offset of the affected spin. A phase-shifted pulse is treated by subtracting the phase shift ϕ from $\alpha(t)$ and adding ϕ to $\chi(t)$.

Once Eqs. 12 or 13 are solved, either analytically or numerically, to obtain $\beta(t)$ and $\gamma(t)$, $\alpha(t)$ is obtained by direct integration of Eq. (7a). The resulting values for t equal to the pulse length are used in Eqs. (1) and (3). For clarity in the following, the pulse length will be denoted τ_p , so that $\alpha(\tau_p)$, $\beta(\tau_p)$, and $\chi(\tau_p)$ are the quantities of interest.

For amplitude-modulated pulses, $d\phi(t)/dt = 0$ and $\omega^+(t) = \omega^-(t) = \omega(t)$, and Eq. (13) becomes:

$$\frac{d^2 y(t)}{dt^2} - \left[\frac{d \ln \omega(t)}{dt} + i\Omega \right] \frac{dy(t)}{dt} + \frac{1}{4} \omega^2(t) y = 0 \quad (14)$$

For a square pulse with $\omega_x(t) = \omega_1$, $\omega_y(t) = 0$, and $\Omega(t) = \Omega$. Equation (14) reduces to:

$$\frac{d^2 y(t)}{dt^2} - i\Omega \frac{dy(t)}{dt} + \frac{1}{4}\omega_1^2 y = 0 \quad (15)$$

with solution:

$$y(t) = e^{i\Omega t/2} \{ \cos(\omega_e t/2) - i(\Omega/\omega_e) \sin(\omega_e t/2) \} \quad (16)$$

Substitution into Eq. (11) gives:

$$f(t) = \sin\theta \tan(\omega_e t/2) \frac{1 + i\cos\theta \tan(\omega_e t/2)}{1 + \cos^2\theta \tan^2(\omega_e t/2)} \quad (17)$$

in which $\theta = \tan^{-1}(\omega_1/\Omega)$ is the tilt angle and $\omega_e = (\Omega^2 + \omega_1^2)^{1/2}$ is the effective field. Using Eqs. (7a) and (10) yields:

$$\begin{aligned} \alpha(\tau_p) &= \tan^{-1}[\cos\theta \tan(\omega_e \tau_p/2)] - \phi \\ \beta(\tau_p) &= \cos^{-1}[\cos^2\theta + \sin^2\theta \cos(\omega_e \tau_p)] \\ \gamma(\tau_p) &= \tan^{-1}[\cos\theta \tan(\omega_e \tau_p/2)] + \phi \end{aligned} \quad (18)$$

The pulse phase ϕ has been added in Eq. (17) to give the most general result. Equations (17) and (18) have been reported previously [4]. The propagator for a square pulse is then:

$$\mathbf{U} = \begin{bmatrix} \cos(\omega_e \tau_p/2) - i\cos\theta \sin(\omega_e \tau_p/2) & -ie^{i\phi} \sin\theta \sin(\omega_e \tau_p/2) \\ -ie^{i\phi} \sin\theta \sin(\omega_e \tau_p/2) & \cos(\omega_e \tau_p/2) + i\cos\theta \sin(\omega_e \tau_p/2) \end{bmatrix} \quad (19)$$

Equations (12–14) assume that the rf field is described by an explicit function. In many cases, the pulse shape is defined by a list of N paired values giving the amplitude and phase (or ω_x and ω_y components) of the ω_1 field applied for a time interval t , with $\tau_p = N t$. The propagator $\mathbf{U}$ of Eq. (1) can be determined by iterative application of Eq. (19) for each step in the pulse shape. The resulting propagator is expressed as [10]

$$\mathbf{U} = \begin{bmatrix} e^{-i[\alpha(\tau_p) + \gamma(\tau_p)]/2} \cos[\beta(\tau_p)/2] & -ie^{i[\alpha(\tau_p) - \gamma(\tau_p)]/2} \sin[\beta(\tau_p)/2] \\ -ie^{-i[\alpha(\tau_p) - \gamma(\tau_p)]/2} \sin[\beta(\tau_p)/2] & e^{i[\alpha(\tau_p) + \gamma(\tau_p)]/2} \cos[\beta(\tau_p)/2] \end{bmatrix} \quad (20)$$

and the parameters $\alpha(\tau_p)$, $\beta(\tau_p)$, and $\gamma(\tau_p)$ are obtained directly from this matrix.

3. Experimental Methods

The NMR spectra of H₂O in a doped water sample (0.1 mg/ml GdCl₃, 0.1% ¹³CH₃OH, 1% H₂O, 99% D₂O; Cambridge Isotope Laboratories, CDLM-5010) were recorded using a pulse sequence 90_φ – CPMG_k – 90_φ – Grad – 90_x – acquire, in which the first two 90° pulses have $\phi = x$ or y phase, k is the number of CPMG blocks, and Grad is a z -gradient pulse to dephase transverse magnetization. Each CPMG block consisted of 8 repetitions of

the element $\tau_{cp}/2-180^\circ-\tau_{cp}$; the 180° pulse separation $\tau_{cp} = 1$ ms. The phases of the 180° pulses were set as described in Results and Discussion. The carrier frequency for the first two 90° pulses and the CPMG blocks was varied between experiments from 0 to 10 kHz in 250 Hz steps. The last 90° pulse was applied on-resonance with the H_2O signal. Pulses were applied with $\omega_1/2\pi = 10$ kHz. The first and last delays in the CPMG sequences were shortened by $2\pi/\tau_{90}$, in which τ_{90} is the 90° pulse length, to account for phase evolution during the first and second 90° pulses. Each experiment was recorded using 8 scans, a recycle delay of 8 s, a spectral width of 25 ppm, and 8,192 complex data points. Experiments were conducted at $T = 300$ K on a Bruker 500 MHz DRX NMR spectrometer with a triple-resonance triple-axis gradient probe.

4. Results and Discussion

The Euler-angle decomposition provides a representation of the propagator that is particularly convenient for NMR spectroscopy, in which z -rotations assume critical prominence. The Euler-angle decomposition is used in the following to establish general properties of amplitude-modulated shaped pulses and repetitive pulse trains, such as the Carr-Purcell-Meiboom-Gill scheme. In particular, the results demonstrate when z -rotations induced by various pulse schemes can be compensated by adjustment of time delays flanking the pulse sequence or minimized by phase alternating schemes.

When Eq. (14) cannot be solved analytically, perturbation theory can be used to determine the limiting properties of a particular rf sequence. Near resonance, the solution to Eq. (14) is assumed to have the form:

$$y(t) = y_0(t) + \varepsilon y_1(t) + \varepsilon^2 y_2(t) + \dots \quad (21)$$

in which $\varepsilon = \Omega/\omega_1$ and ω_1 is the maximum strength of the rf field. Substituting for $y(t)$ and equating terms of the same order in ε transforms Eq. (14) into a system of equations:

$$\begin{aligned} \frac{d^2 y_0(t)}{dt^2} - \frac{d \ln \omega(t)}{dt} \frac{dy_0(t)}{dt} + \frac{1}{4} \omega^2(t) y_0(t) &= 0 \\ \frac{d^2 y_n(t)}{dt^2} - \frac{d \ln \omega(t)}{dt} \frac{dy_n(t)}{dt} + \frac{1}{4} \omega^2(t) y_n(t) &= i \omega_1 \frac{dy_{n-1}(t)}{dt} \quad (n \geq 1) \end{aligned} \quad (22)$$

The first equation is simply the result for an on-resonance pulse and has the solution $y_0(t) = \cos[\delta(t)/2]$, in which:

$$\delta(t) = \int_0^t \omega(t') dt' \quad (23)$$

is the instantaneous accumulated rotation angle. The solutions of Eq. (22) for $n \geq 1$ have the form $y_n(t) = u_n(t)y_+(t) + v_n(t)y_-(t)$, in which $y_{\pm}(t) = \exp[\pm i\delta(t)]$ and $u_n(t)$ and $v_n(t)$ satisfy the equations:

$$\begin{aligned} \frac{du_n(t)}{dt} y_+(t) + \frac{dv_n(t)}{dt} y_-(t) &= 0 \\ \frac{du_n(t)}{dt} \frac{dy_+(t)}{dt} + \frac{dv_n(t)}{dt} \frac{dy_-(t)}{dt} &= i \omega_1 \frac{dy_{n-1}(t)}{dt} \end{aligned} \quad (24)$$

Substituting for $y(t)$ in Eq. (8) and solving for $f(\tau_p)$ to second-order in ε yields:

$$f(\tau_p) \approx \tan \left[\frac{\delta(\tau_p)}{2} \right] \left\{ 1 + \frac{i\varepsilon}{\sin\delta(\tau_p)} S(\tau_p) - \frac{\varepsilon^2}{2\delta(\tau_p)} \left[S^2(\tau_p) \tan \left[\frac{\delta(t)}{2} \right] + S(\tau_p)C(\tau_p) + G(\tau_p) \right] \right\} \quad (25)$$

in which,

$$\begin{aligned} S(\tau_p) &= \omega_1 \int_0^{\tau_p} \sin[\delta(t)] dt \\ C(\tau_p) &= \omega_1 \int_0^{\tau_p} \cos[\delta(t)] dt \\ G(\tau_p) &= \omega_1^2 \int_0^{\tau_p} \int_0^{t'} \sin[\delta(t') - \delta(t)] dt' dt \end{aligned} \quad (26)$$

$S(\tau_p)$ is the integrated y-magnetization over the duration of the rf pulse and $\delta(\tau_p)$ is the nominal rotation angle of the pulse. Notably, the integrals in Eqs (25) and (26) depend only on the pulse shape and not on the resonance offset. The second-order expansion gives:

$$\begin{aligned} \tan[\gamma(\tau_p)] &\approx \varepsilon S(\tau_p) / \sin\delta(\tau_p) \\ \cos[\beta(\tau_p)] &\approx \cos\delta(\tau_p) + \frac{\varepsilon^2}{2} [S(\tau_p)C(\tau_p)\sin\delta(\tau_p) + G(\tau_p)\sin\delta(\tau_p) - S(\tau_p)\cos\delta(\tau_p)] \end{aligned} \quad (27)$$

and the next correction to $\tan[\gamma(\tau_p)]$ is of order ε^3 .

If $\alpha(\tau_p)$ and $\gamma(\tau_p)$ are proportional to Ω over some bandwidth near resonance for a particular rf pulse, then the pulse can be treated as a sequence $\tau_a - \mathbf{R}_\phi[\beta(\tau_p)] - \tau_\gamma$, in which $\mathbf{R}_\phi(\beta)$ is a rotation by an angle β around an axis with phase ϕ in the transverse plane, $\tau_a = \alpha(\tau_p)/\Omega$ and $\tau_\gamma = \gamma(\tau_p)/\Omega$. Using $\tan[\gamma(\tau_p)] \sim \gamma(\tau_p)$ near resonance yields,

$$\tau_\gamma \approx -\frac{1}{\sin\delta(\tau_p)} \int_0^{\tau_p} \sin[\delta(t)] dt \quad (28)$$

When the average y-magnetization is zero, then $\gamma(\tau_p) = 0$ and no phase correction is needed following the pulse. An analogous expression for τ_a is obtained by time-reversing the pulse:

$$\tau_a \approx \frac{1}{\sin\tilde{\delta}(\tau_p)} \int_0^{\tau_p} \sin[\tilde{\delta}(t)] dt \quad (29)$$

in which

$$\tilde{\delta}(t) = \int_{\tau_p-t}^{\tau_p} \omega(t') dt' \quad (30)$$

The above results suggest that all amplitude-modulated $\pi/2$ pulses will have $\alpha(\tau_p)$ and $\gamma(\tau_p)$ proportional to Ω over at least some bandwidth $|\Omega/\omega_1| \ll 1$ and allow direct calculation of τ_a and τ_γ as integrals over the rf field amplitude function.

Far from resonance, a perturbation solution for $f(t)$ is directly obtained from the Riccati equation by writing

$$f(t) = f_0(t) + \varepsilon f_1(t) + \varepsilon^2 f_2(t) + \varepsilon^3 f_3(t) \dots \quad (31)$$

in which $\varepsilon = \omega_1/\Omega$. By substitution into Eq. (9), the values of $f_0(t) = f_2(t) = f_4(t) = 0$ and

$$\begin{aligned} \frac{df_1(t)}{dt} &= i\Omega f_1(t) + \frac{\Omega}{2\omega_1} \omega(t) \\ \frac{df_3(t)}{dt} &= i\Omega f_3(t) + \frac{\Omega}{2\omega_1} \omega(t) f_1^2(t) \end{aligned} \quad (32)$$

Solving these two equations yields

$$\begin{aligned} f_1(\tau_p) &= \frac{\Omega}{2\omega_1} e^{i\Omega\tau_p} \int_0^{\tau_p} e^{-i\Omega t} \omega(t) dt \\ f_3(\tau_p) &= \frac{\Omega^3}{8\omega_1^3} e^{i\Omega\tau_p} \int_0^{\tau_p} e^{i\Omega t} \omega(t) \left[\int_0^t e^{-i\Omega t'} \omega(t') dt' \right]^2 dt \end{aligned} \quad (33)$$

Thus, to second order in ω_1/Ω ,

$$\cos\beta(\tau_p) = 1 - \frac{1}{2} \left| \int_0^{\tau_p} e^{-i\Omega t} \omega(t) dt \right|^2 \quad (34)$$

yielding the first-order estimate:

$$\beta(\tau_p) = \left| \int_0^{\tau_p} e^{-i\Omega t} \omega(t) dt \right| \quad (35)$$

The z -rotation angle $\gamma(\tau_p)$ is given by

$$\begin{aligned} \gamma(\tau_p) &= \text{Arg}[f(\tau_p)] = \Omega\tau_p/2 + \text{Arg} \left[\int_0^{\tau_p} e^{-i\Omega(t-\tau_p/2)} \omega(t) dt \right] \\ &+ \text{Arg} \left[1 + \int_0^{\tau_p} e^{i\Omega t} \omega(t) \left[\int_0^t e^{-i\Omega t'} \omega(t') dt' \right]^2 dt / 4 \int_0^{\tau_p} e^{-i\Omega t} \omega(t) dt \right] \end{aligned} \quad (36)$$

As $\Omega \rightarrow \infty$, $\gamma(\tau_p) \rightarrow \Omega\tau_p/2$; consequently, the second term in the above equation is negligible and

$$\gamma(\tau_p) - \Omega\tau_p/2 = \text{Im} \left[\int_0^{\tau_p} e^{i\Omega t} \omega(t) \left[\int_0^t e^{-i\Omega t'} \omega(t') dt' \right]^2 dt / 4 \int_0^{\tau_p} e^{-i\Omega t} \omega(t) dt \right] \quad (37)$$

The square pulse is analyzed first to illustrate the properties of the perturbation solutions. Close to resonance, Eq. (27) yields:

$$\alpha(\tau_p) = \gamma(\tau_p) \left(\frac{\Omega}{\omega_1} \right) \tan(\psi/2) \\ \cos\beta(\tau_p) \approx \cos\psi + \frac{\varepsilon^2}{2} [(1 - \cos\psi)(2 - \cos^2\psi) - \psi \sin\psi] \quad (38)$$

in which the nominal rotation angle $\psi = \omega_1 \tau_p$. Thus, a square pulse with x -phase can be regarded near resonance as an x -rotation preceded and followed by a delay $\tau = \tan(\omega_1 \tau_p/2)/\omega_1 = \tau_p \tan(\psi/2)/\psi$. If $\omega_1 \tau_p = \pi/2$ for a nominal 90° pulse, then $\tau = 2\tau_p/\pi$ as also can be shown by standard techniques [1]. Far from resonance, Eqs. (35) and (37) yield:

$$\alpha(\tau_p) = \gamma(\tau_p) = \Omega \tau_p / 2 + \frac{\omega_1^2}{4\Omega^2} \{ \Omega \tau_p - \sin(\Omega \tau_p) \} \approx \omega_e \tau_p / 2 - \frac{\omega_1^2}{4\Omega^2} \sin(\Omega \tau_p) \\ \beta(\tau_p) = \frac{2\omega_1}{\Omega} \left[\sin^2(\Omega \tau_p / 2) + \frac{\omega_1^2}{4\Omega^2} \{ \Omega \tau_p - \sin(\Omega \tau_p) \} \right]^{1/2} \approx \frac{2\omega_1}{\Omega} \sin(\omega_e \tau_p / 2) \quad (39)$$

and the third-order term has been included in the expression for β for increased accuracy (the first-order result replaces ω_e by Ω). The propagator is

$$\mathbf{U} \approx \exp[-i\gamma(\tau_p)I_z] \exp\left[-i\frac{2\omega_1}{\Omega} \sin(\omega_e \tau_p / 2) I_x\right] \exp[-i\gamma(\tau_p)I_z] \\ = \exp[-i2\gamma(\tau_p)I_z] \exp\left[-i\frac{2\omega_1}{\Omega} \sin(\omega_e \tau_p / 2) \{I_x \cos(\gamma(\tau_p)) - I_y \sin(\gamma(\tau_p))\}\right] \quad (40) \\ \approx \exp[-i2\gamma(\tau_p)I_z] \exp\left[-i\frac{\omega_1}{\Omega} \{I_x \sin(\omega_e \tau_p) - I_y (1 - \cos(\omega_e \tau_p))\}\right]$$

In the absence of the pulse, transverse magnetization of the off-resonance spin would acquire a phase $\Omega \tau_p$; as shown by the first factor of Eq. (40), the phase acquired during the pulse is $2\gamma(\tau_p)$ so that the off-resonance phase error becomes:

$$\phi_{NR} = \frac{\omega_1^2}{2\Omega^2} \{ \Omega \tau_p - \sin(\Omega \tau_p) \} \quad (41)$$

This expression approaches the well-known result $\phi_{NR} = \omega_1^2 \tau_p / (2\Omega)$ of McCoy and Mueller [11] when $\Omega \tau_p \gg 1$, but is more accurate for intermediate cases. The second factor is a rotation by an angle around an axis in the transverse plane that is phase-shifted by an angle $\chi = \tan^{-1}[(\cos(\omega_e \tau_p) - 1)/\sin(\omega_e \tau_p)] = -\omega_e \tau_p / 2$. In many applications [1], the amplitude of the ω_1 field is adjusted to yield the rotation angles $\omega_1 \tau_p$ on-resonance and $2n\pi$ at an offset frequency Ω ; consequently, $\beta(\tau_p) = 0$. The expressions given in Eqs. (35) and (37), although more computationally demanding, are generally more accurate than the analogous expressions of McCoy and Mueller [11] and are related to expressions obtained from average Hamiltonian theory by Warren [3]. For illustration, the values of $\beta(\tau_p)$, and $\gamma(\tau_p)$ for square x -pulses are shown in Fig. 1.

The more useful applications of the above formalism are to rf pulses with time-varying parameters. EBURP-2 [12] and Q5 [13] pulses are widely used band-selective 90° excitation pulses. The results for $\alpha(\tau_p)$, $\beta(\tau_p)$, and $\gamma(\tau_p)$, calculated from the analytical forms of the pulse shapes by solution of Eqs. (14) for $y(t)$, are shown in Figs. 2 and 3; identical results are obtained by discretizing the pulse shapes and applying Eqs. (19) and (20). The values of

$\alpha(\tau_p)$ and $\gamma(\tau_p)$ are approximately linear functions of Ω for a bandwidth of $\pm 0.3 \Omega/\omega_1$ for the EBURP-2 pulse and $\pm 0.4 \Omega/\omega_1$ for the Q5 pulse. Thus, both pulses can be described within their bandwidths by the sequence $\tau_a - 90^\circ_x - \tau_\gamma$ with $\tau_a = 0.718 \tau_p$ and $\tau_\gamma \approx 0$ for the EBURP-2 pulse and $\tau_a = \tau_\gamma \approx 0$ for the Q5 pulse, calculated using Eqs. (28) and (29). A numerical fit to the value of $\alpha(\tau_p)$ near resonance in Fig. 2a yields an estimate of $\tau_a = 0.70$. The value of τ_a for the EBURP-2 pulse agrees well with the fitted value of $0.67 \tau_p$ reported previously from numerical fitting of the phase of transverse magnetization following the pulse [8]. The calculated near-resonance z -rotation angles for the Q5 pulse are $\alpha(\tau_p) = 0.013 \Omega \tau_p$ and $\gamma(\tau_p) = -0.076 \Omega \tau_p$; thus, as also illustrated by Figs. 3b and 3c, slightly better phase performance for excitation of $M_z \rightarrow M_y$ is expected for the time-reversed Q5 pulse. Results for τ_a and τ_γ are given in Table 1 for these and other common pulse shapes.

A number of novel pulse shapes with exceptional properties have been determined by optimal control methods [14]. Fig. 4a shows the pulse shape developed by Li and coworkers for broadband excitation with minimal pulse power requirements [15]. The excitation profile is shown in Fig. 4b. The corresponding Euler rotation angles determined from Eq. (26) are shown in Fig. 4c–d. The results show that over the excitation bandwidth of ± 20 kHz for $\omega_1 = 20$ kHz, the pulse can be regarded as the sequence $\tau - 90^\circ_x$, with $\tau = 0.87 \tau_p$. Reversing the pulse shape profile exchanges $\alpha(\tau_p; \Omega) = -\gamma(\tau_p; -\Omega)$, $\gamma(\tau_p) = -\alpha(\tau_p; -\Omega)$, and $\beta(\tau_p; \Omega) = \beta(\tau_p; -\Omega)$; thus, the time-reversed pulse can be regarded as the sequence $90^\circ_x - \tau$, allowing broadband transformations from y - to z -magnetization. The Euler angle representation allows convenient representation of the properties of pulses with complex rf profiles for comparison with other pulse shapes, e.g. comparing Figs. 2–4.

The formalism is also applicable to pulse trains consisting of pulse-interrupted-free-precession sequence blocks:

$$\tau_1 - P(\omega_{11}, \tau_{p1}, \phi_1) - \tau_2 - P(\omega_{12}, \tau_{p2}, \phi_2) - \tau_3$$

in which τ_n is a time delay and $P(\omega_{1n}, \tau_{pn}, \phi_n)$ is a square pulse applied with rf field ω_{1n} , length τ_{pn} , and phase ϕ_n , is commonly encountered in NMR spectroscopy. Using Eqs. (3), (19), and (20) yields the propagator for this pulse sequence as:

$$U = \exp[-i(\Omega\tau_3 + \gamma_2 + \gamma)I_z] \exp[-i\beta I_x] \exp[-i(\Omega\tau_1 + \alpha_1 + \alpha)I_z] \quad (42)$$

in which α_n , β_n , and γ_n are given in Eq. (18) for the n th pulse,

$$\begin{aligned} \alpha &= \tan^{-1} \left[\frac{2\sin\beta_2 \tan(\delta/2)}{\sin(\beta_1 + \beta_2) \cos^2(\delta/2) + \sin(\beta_1 - \beta_2) \tan^2(\delta/2)} \right] \\ \beta &= \cos^{-1} \left[\cos(\beta_1 + \beta_2) \cos^2(\delta/2) + \cos(\beta_1 - \beta_2) \sin^2(\delta/2) \right] \\ \gamma &= \tan^{-1} \left[\frac{2\sin\beta_1 \tan(\delta/2)}{\sin(\beta_1 + \beta_2) \cos^2(\delta/2) - \sin(\beta_1 - \beta_2) \tan^2(\delta/2)} \right] \end{aligned} \quad (43)$$

and $\delta = \alpha_2 + \Omega \tau_2 + \gamma_1 = \delta_0 - \phi_2 + \phi_1$. In the limit that $\tau_2 \rightarrow 0$ ($\delta \rightarrow \alpha_2 + \gamma_1$), Eq. (43) yields the Euler angle composition rule [16], which defines the effective Euler angles from two successive rotations.

If the two pulses are applied with values of ω_1 and τ_p (but potentially different phases), then a simpler result is obtained:

$$\begin{aligned}\alpha &= \gamma = \tan^{-1} \left[\frac{\tan(\delta/2)}{\cos\beta_1} \right] \\ \beta &= \cos^{-1} \left[1 - 2\sin^2\beta_1 \cos^2(\delta/2) \right]\end{aligned}\quad (44)$$

The Carr-Purcell-Meiboom-Gill (CPMG) sequence, $\tau - \pi_{\phi_1} - 2\tau - \pi_{\phi_2} - \tau$, with $\omega_1 \tau_p = \pi$ is an example of a pulse sequence with identical pulse lengths. Application of Eq. (44) gives:

$$\mathbf{U}_{\phi_2\phi_1} = \exp[-i\{\eta + (3\phi_2 - \phi_1)/2\}I_z] \exp[-i\beta I_x] \exp[-i\{\eta + (\phi_2 - 3\phi_1)/2\}I_z] \quad (45)$$

in which

$$\eta = \tan^{-1} \left[\frac{\sin\delta}{\cos\delta - \tan^2(\beta_1/2)} \right] \quad (46)$$

The conventional two-pulse CPMG pulse sequence element has the propagator $\mathbf{U}_{xx}$ with $\phi_1 = \phi_2 = 0$. Yip and Zuiderweg [17] proposed a four-pulse CPMG sequence, $\tau - \pi_x - 2\tau - \pi_x - 2\tau - \pi_y - 2\tau - \pi_y - \tau$. A propagator for this sequence is given by $\mathbf{U} = \mathbf{U}_{yy}\mathbf{U}_{xx}$, in which:

$$\begin{aligned}\mathbf{U}_{xx} &= \exp[-i\eta_- I_z] \exp[-i\beta_+ I_x] \exp[-i\eta_- I_z] \\ \mathbf{U}_{yy} &= \exp[-i\eta_+ I_z] \exp[i\beta_- I_x] \exp[-i\eta_+ I_z]\end{aligned}\quad (47)$$

and

$$\begin{aligned}\eta_{\pm} &= \tan^{-1} \left[\frac{\sin\delta_0}{\cos\delta_0 \pm \tan^2(\beta_1/2)} \right] \\ \beta_{\pm} &= \cos^{-1} \left[1 - \sin^2\beta_1 (1 \pm \cos\delta_0) \right]\end{aligned}\quad (48)$$

This propagator can be recast by the same approach embodied in Eqs. (42) and (43) to give:

$$\mathbf{U}_{yy}\mathbf{U}_{xx} = \exp[-i\hat{\gamma}I_z] \exp[-i\hat{\beta}I_x] \exp[-i\hat{\alpha}I_z] \quad (49)$$

in which

$$\begin{aligned}\hat{\alpha} &= \eta_- + \tan^{-1} \left[\frac{-2\sin\beta_- \tan\bar{\eta}}{\sin(\beta_+ + \beta_-) \tan^2\bar{\eta} + \sin(\beta_+ - \beta_-)} \right] \\ \hat{\beta} &= \cos^{-1} \left[1 - 2\sin^2\bar{\beta} \sin^2\bar{\eta} - 2\sin^2\Delta\bar{\beta} \cos^2\bar{\eta} \right] \\ \hat{\gamma} &= \eta_+ + \tan^{-1} \left[\frac{-2\sin\beta_+ \tan\bar{\eta}}{\sin(\beta_+ + \beta_-) \tan^2\bar{\eta} - \sin(\beta_+ - \beta_-)} \right]\end{aligned}\quad (50)$$

$\beta = (\beta_- + \beta_+)/2$, $\bar{\beta} = (\beta_+ - \beta_-)/2$, and $\bar{\eta} = (\eta_- + \eta_+)/2$. Illustrative calculations of the rotation angles for the two CPMG variants are shown in Figs. 5a, b. The major difference between the sequences is that for the Yip and Zuiderweg scheme, $\hat{\alpha} \approx -\hat{\gamma}$, with an absolute difference of 0.5° for $-0.3 \Omega/\omega_1$ to 0.3 for the parameters used for Fig. 5. Thus, the propagator for the complete CPMG train, consisting of n repetitions of the four-step cycle simplifies to

$$(\mathbf{U}_{yy}\mathbf{U}_{xx})^n \approx \exp[-i\hat{\gamma}I_z] \exp[-in\hat{\beta}I_x] \exp[-i\hat{\alpha}I_z] \quad (51)$$

and, unlike the conventional sequence, the effects of the z -rotations are not cumulative over the n cycles.

Equation (49) indicates that the eight-pulse phase alternating scheme formed by concatenating the Yip and Zuiderweg four-pulse scheme and its phase-inverted counterpart, yielding the phases $x, x, y, -y, -x, -x, -y, y$, has a propagator described by:

$$\begin{aligned} \mathbf{U} &= \mathbf{U}_{yy} \mathbf{U}_{xx} \mathbf{U}_{yy} \mathbf{U}_{xx} = \mathbf{U}_{yy} \mathbf{U}_{xx} \mathbf{U}_{yy} \mathbf{U}_{xx} \\ &= \exp[-i\hat{\gamma}I_z] \exp[i\hat{\beta}I_x] \exp[-i\hat{\alpha}I_z] \exp[-i\hat{\gamma}I_z] \exp[-i\hat{\beta}I_x] \exp[-i\hat{\alpha}I_z] \\ &\approx \exp[-i\hat{\gamma}I_z] \exp[i\hat{\beta}I_x] \exp[-i\hat{\beta}I_x] \exp[-i\hat{\alpha}I_z] \\ &\approx \exp[-i\hat{\gamma}I_z] \exp[-i\hat{\alpha}I_z] \\ &\approx \mathbf{E} \end{aligned} \quad (52)$$

in which $\mathbf{E}$ is the identity operator. The calculations shown in Fig. 5c demonstrate the effective x -rotation is reduced by two orders of magnitude in the eight-pulse scheme compared to the four-pulse scheme shown in Fig. 5a and nearly an order of magnitude smaller than the XY-8 scheme [18] (not shown). The residual x -rotation is 1° over the range $-0.3 \Omega/\omega_1$ 0.3 (and 1.7° for a variation in ω_1 of $\pm 10\%$); consequently the two z -rotations shown in Fig. 5d nearly cancel to yield a propagator proportional to the identity operator. Thus, the proposed eight-pulse phase alternating scheme should refocus transverse magnetization with arbitrary initial phase more accurately than XY-8 (the conventional or Yip and Zuiderweg schemes do not efficiently refocus magnetization with initial y -phase). Figs. 6a and 6b show the numerically calculated magnetization after a single cycle of each refocusing scheme as a function of resonance offsets. For fair comparison, each cycle consists of eight pulses for all schemes.

The performance of the different refocusing schemes also depends on the extent to which phase errors accumulate as more than one cycle of the CPMG pulse train is applied. In particular, the residual x -phase rf fields in the conventional and Yip and Zuiderweg schemes dominate small non-commuting terms in the Hamiltonian; in contrast, sequences proportional to the identity operator, like the proposed sequence or XY-8, do not have this property and can be expected to be more sensitive to accumulated effects. The magnitudes of refocused magnetization have been calculated following 1 – 100 cycles of all four refocusing schemes. Figs. 6c and 6d show the average refocused transverse magnetization. The Yip and Zuiderweg scheme, as predicted from Eq. (51) has the largest bandwidth ($\sim 0.35|\Omega/\omega_1|$). The proposed eight-pulse scheme has a bandwidth ($\sim 0.16|\Omega/\omega_1|$) substantially larger than the XY-8 scheme ($\sim 0.1|\Omega/\omega_1|$) both in the absence and the presence of rf inhomogeneity (Figs. 6c–6f). Only the proposed eight-pulse scheme and XY-8 refocus y -magnetization. Experimental validation of these predictions is shown in Fig. 7. As shown in Fig. 7a, both the Yip and Zuiderweg and the proposed CPMG sequences conserve $>95\%$ of both initial x - and y -magnetization at resonance offsets up to $0.5|\Omega/\omega_1|$ for a single cycle consisting of eight pulses (and a total time of 8 ms). The bandwidth of the Yip and Zuiderweg scheme is largely maintained as the number of cycles in the pulse train increases,

while the bandwidth for the proposed sequence is reduced to $0.3|\Omega/\omega_1|$ for 10 cycles (a total time of 80 ms). As shown in Fig. 7b, the proposed CPMG sequence is equally efficient in refocusing x- or y-magnetization. The bandwidth of the proposed sequence, consistent with the calculations shown in Fig. 6 is larger than that for the XY-8 sequence, as shown in Fig. 7c–e for increasing numbers of cycles.

Additional insights into the relative performance of the XY-8 and proposed schemes over many cycles can be gained from calculation of effective Hamiltonian. These calculations were performed using exact effective Hamiltonian theory (EEHT) [19, 20] and expanded to fifth order with respect to resonance offset. For the XY-8 scheme,

$$H_{eff} = \left[-\frac{0.5r_{cp}+0.25}{r_{cp}+1}\varepsilon^4 - \frac{0.393r_{cp}+0.785r_{cp}^2}{r_{cp}+1}\varepsilon^5 \right] \omega_1 I_x + \left[-\frac{0.5r_{cp}+0.25}{r_{cp}+1}\varepsilon^4 + \frac{0.393r_{cp}+0.785r_{cp}^2}{r_{cp}+1}\varepsilon^5 \right] \omega_1 I_y + \left[-\frac{r_{cp}+0.5}{r_{cp}+1}\varepsilon^5 \right] \omega_1 I_z + O(\varepsilon^6) \quad (53)$$

For the proposed eight-pulse scheme,

$$H_{eff} = -\frac{r_{cp}+0.5}{r_{cp}+1}\varepsilon^5 \omega_1 I_z + O(\varepsilon^6) \quad (54)$$

in which $\varepsilon = \Omega/\omega_1$, $r_{cp} = \tau_{cp}/\tau_{180}$, τ_{cp} is the spacing between pulses, and τ_{180} is the length of the 180° pulse. The EEHT results show that the proposed eight-pulse scheme gives superior performance over XY-8, regardless of the number cycles applied, because the z-components of the effective Hamiltonians are identical in the fifth order expansion, whereas the new scheme compensates x- and y- components to higher order than the XY-8 scheme. Although simple and more intuitive, representation of effective Hamiltonian by power series is less accurate when the value of r_{cp} is large. Figure 8 shows the exact effective Hamiltonian, without truncation to powers, as a function of resonance offsets at different r_{cp} values. When r_{cp} is large, the effective Hamiltonians oscillate at high frequency outside the effective bandwidth and therefore cannot be well represented by power series expansion. However, the numerical representations of effective Hamiltonian obtained from its exact expression are consistent with the numerical results shown in Fig. 6. The performance of the proposed eight-pulse scheme is not significantly altered by expanding into a 16-step scheme $\overline{RRRR}$ in which $R = U_{xx}U_{y-}$ and the bar indicates phase inversion. Thus, the improved performance of the proposed scheme is not simply a consequence of imposing a supercycle, as utilized in decoupling schemes [1]. The above considerations indicate that the Yip and Zuiderweg phase-alternation scheme has a superior bandwidth than the other schemes if initial x-magnetization (i.e. magnetization with the same phase as the first 180° pulse) is to be refocused, but that the proposed scheme has the best performance if both x-magnetization and y-magnetization (orthogonal to the first pulse) must be retained. The Yip and Zuiderweg scheme is the choice for most CPMG relaxation dispersion experiments [21] and the proposed scheme for applications such as CPMG-INEPT polarization transfers [22, 23] and a subset of CPMG relaxation dispersion experiments, in which the starting magnetization is of arbitrary phase [24].

5. Conclusion

The Euler-angle rotation operator factorization of the propagator for time-varying rf pulses and pulse-interrupted-free-precession trains provides insights into performance that are not as easily discerned by average Hamiltonian theory or by numerical calculation of the evolution of magnetization through the pulse. The Euler-angle representation is particularly useful in determining whether a shaped pulse or pulse train can be represented over some bandwidth by a sequence $\tau_1 - \mathbf{R}(\beta) - \tau_2$, allowing phase evolution during the pulse to be compensated by adjusting time periods prior or subsequent to the pulse. Explicit solutions for the Euler rotation angles have been derived using perturbation theory near- and off-resonance; the resulting expressions are useful especially for characterizing phase evolution of magnetization during shaped pulses. The Euler-angle approach also is powerful in analyzing repetitive pulse trains, such as the CPMG sequence and has been used to identify an eight-step phase alternating scheme that performs better than the XY-8 scheme in refocusing magnetization orthogonal to the phase of the first pulse in the CPMG train.

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Highlights

- The rotation operator formalism is applied to shaped pulses and pulse-interrupted-free-precession sequences
- The formalism allows convenient assessment of the phase evolution properties of shaped pulses
- An approach is demonstrated for iteratively simplifying the propagators for pulse trains
- The performance of a novel Carr-Purcell-Meiboom-Gill sequence is demonstrated

Figure 1.

Euler angles (a, c, e) $\alpha(\tau_p) = \gamma(\tau_p)$ and (b, d, f) $\beta(\tau_p)$ and for a square (a, b) 90°, (c, d) 270°, and (e, f) 60° x-pulse are shown as a function of the offset parameter Ω/ω_1 . The limiting (red) near-resonance ($\Omega/\omega_1 = 1$) and (blue) off-resonance ($\Omega/\omega_1 = 1$) values also are depicted.

Figure 2.

Euler angles (a) $\alpha(\tau_p)$, (b) $\beta(\tau_p)$, and (c) $\gamma(\tau_p)$ for a EBURP-2 pulse are shown as a function of the ratio of resonance offset and B_1 field, Ω/ω_1 . (red) The limiting near-resonance linear dependence of $\alpha(\tau_p)$ over the bandwidth $\pm 0.3\Omega/\omega_1$ is shown.

Figure 3. Euler angles (a) $\alpha(\tau_p)$, (b) $\beta(\tau_p)$, and (c) $\gamma(\tau_p)$ for a Q5 pulse are shown as a function of the ratio of resonance offset and B_1 field, Ω/ω_1 .

Figure 4.

Minimum-energy broadband excitation pulse. (a) The (black) $\omega_x(t)$ and (red) $\omega_y(t)$ components of the pulse shape are shown. (b) The excitation profile for z-magnetization is shown as a function of the resonance offset Ω . (c) The Euler angles (black) $\alpha(\tau_p)$ and (red) $\gamma(\tau_p)$ and (d) $\beta(\tau_p)$ are shown as a function of the resonance offset Ω . The pulse had a length of 100 μ s and $\omega_1/(2\pi) = 20$ kHz.

Figure 5.

CPMG pulse sequences. (a) The effective x -rotation angle $\hat{\beta}$ for (black) conventional two-pulse and (red) Yip and Zuiderweg [17] four-pulse phase alternating scheme. (b) The effective z -rotation angles $\hat{\alpha}$ for the (black) conventional and (red) $\hat{\alpha}$ and (blue) $\hat{\gamma}$ for the Yip and Zuiderweg schemes. The (c) effective x -rotation angle $\hat{\beta}$ and (d) (red) $\hat{\alpha}$ and (blue) $\hat{\gamma}$ for the eight-pulse phase alternating scheme. All calculations used $\omega_1/2\pi = 6250$ Hz, $\tau_{cp} = 0.5$ ms, in which τ_{cp} is the spacing between π pulses.

Figure 6.

Refocused transverse magnetization as a function of the ratio of resonance offset and B_1 field, Ω/ω_1 . Plots show refocused (b,d,f) x -magnetization or (a,c,e) y -magnetization following CPMG pulse trains beginning with initial (b,d,f) x -magnetization or (a,c,e) y -magnetization. Panels (a) and (b) show the refocused magnetization after one cycle of CPMG pulse train. Panels (c,d,e,f) show the refocused magnetization after n cycles, averaged over $n = 1$ to 100. For panels (e) and (f), 10% rf inhomogeneity (FWHM) was included in the calculation. Each cycle consists of 8 pulses for all four schemes. The color coding is (blue) conventional x -phase, (black) Yip and Zuiderweg phase alternating scheme, (red) proposed eight-pulse phase alternating scheme, and (green) XY-8 scheme. All calculations used $\omega_1/2\pi = 2500$ Hz, $\tau_{cp} = 1.25$ ms, in which τ_{cp} is the spacing between π pulses. The calculations were performed using the software package SIMPSON [25].

Figure 7.

CPMG performance demonstrated from normalized intensities for the ^1H resonance of H_2O in a doped water sample. (a) Refocused x -magnetization for the (black) proposed and (red) Yip and Zuiderweg phase alternating scheme for (circles) 8 ms, (squares) 40 ms, and (triangles) 80 ms pulse trains, corresponding to 1, 5, and 10 repetitions of an 8-pulse CPMG block, as described in Experimental Methods. (b) Refocused (black) x -magnetization and (red) y -magnetization for the proposed eight-pulse phase alternating scheme for (circles) 8 ms, (squares) 40 ms, and (triangles) 80 ms pulse trains. (c–e) Refocused x -magnetization for (red, circle) the proposed eight-pulse scheme and (green, square) the XY-8 scheme for (c) 8 ms, (d) 40 ms, and (e) 80 ms pulse trains overlaid onto the x -magnetization from numerical simulations using (black) the proposed scheme and (blue) the XY-8 scheme. 10% rf inhomogeneity (FWHM) was included in the calculations. The magnetizations in panels (c)–(d) were normalized to the values at zero resonance offset for clarity. The relative performance of the proposed and XY-8 schemes for y -magnetization are similar to the performance for x -magnetization and is not shown. The Yip and Zuiderweg scheme does not refocus orthogonal y -phase magnetization and results are not shown for this sequence.

Figure 8.

The x -, y - and z -components of effective Hamiltonians from EEHT calculations for (a,b,c) the XY-8 and (d,e,f) proposed 8-pulse schemes, multiplied by the cycle time, τ_c . The product reflects the residual x -, y - and z -rotations each cycle. The calculations were performed at τ_{cp}/τ_{180} values of (red) 0, (green) 1, (blue) 10 and (magenta) 100.

Table 1

z-Rotation Scaling Factors for Shaped Pulses

Pulse	τ_a/τ_p	τ_y/τ_p
Square	0.637	0.637
Sinc ¹	0.597	0.597
Gaussian ²	0.589	0.589
E-BURP2	0.718	0
Q5	0	0

¹Defined as the center lobe of the sinc function.²Truncated at an amplitude of $0.0471 \omega_1$.