Modern methods in experimental physics:
site-directed spin labeling EPR

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Solution Set 1

Problem 1: On- and off-resonance pulses

On-resonance pulses

a. The magnetization nutates on a cone around $\vec{B}_1 = \dfrac{\omega_1}{\gamma}\vec{e}_y$. The nutation frequency is $\omega_1/2\pi = 100$ kHz. With the pulse length of $\tau = 2.5\ \mu s$ we obtain the flip angle $\beta_1 = \omega_1\tau = 90° = 1.57$ rad.

b. The resulting magnetization vector $\vec{M}(\tau)$ in the rotating frame after the 2.5 μs pulse is obtained by calculating the nutation of $\vec{M}(0)$ at t=τ using: $\vec{M}(\tau) = \mathbf{R}_y(\beta_1)\vec{M}(0)$ with the flip angle $\beta_1 = \omega_1\tau = \pi/2$ rad.

$$\mathbf{R}_y(\beta_1) = \begin{pmatrix} \cos\beta_1 & 0 & \sin\beta_1 \\ 0 & 1 & 0 \\ -\sin\beta_1 & 0 & \cos\beta_1 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix} \quad (1)$$

giving $\vec{M}(\tau) = \mathbf{R}_y(\beta_1)\vec{M}(0) = (1,0,0)$

Off-resonance pulses

a. The magnetization nutates on a cone around the effective field vector given by $\vec{B}_{\text{eff}} = \vec{B}_1 + \Delta\vec{B} = \dfrac{\omega_1}{\gamma}\vec{e}_y + \dfrac{\Omega}{\gamma}\vec{e}_z$. The nutation frequency is $\omega_{\text{eff}}/2\pi = \sqrt{\omega_1^2 + \Omega^2}/2\pi = 141.4$ kHz. With the pulse length of $\tau = 2.5\ \mu s$ we then obtain the effective flip angle $\beta_{\text{eff}} = \omega_{\text{eff}}\tau = 127° = 2.22$ rad.

   The angle between the effective magnetic field and and the z-axis is $\theta = \arctan(|\omega_1/\Omega|) = \pi/4 = 45°$.

   For the on-resonance case, the nutation frequency is $\omega_1/2\pi = 100.0$ kHz. With the pulse length of $\tau = 2.5\ \mu s$ we would obtain a $\pi/2$ pulse, characterized by a flip angle $\beta = \omega_1\tau = 90° = 1.57$ rad.

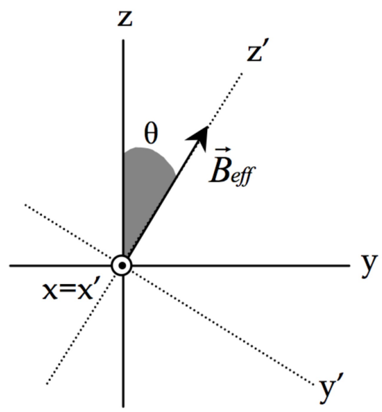

Figure 1: Orientation of the effective magnetic field in the two coordinate frames.

b. For the off-resonance case, to make the calculations easier we study the precession of the magnetization vector in a tilted frame in such a way that its z-axis is defined by the effective field (see figure 2). The rotation matrix transforming vectors to this new coordinate system is

$$\mathbf{R}_x(\theta) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix} \tag{2}$$

The thermal equilibrium magnetization $\vec{M}(0)$ in this tilted frame is

$$\vec{M}'(0) = \mathbf{R}_x(\theta)\vec{M}(0) = (0, -\sin\theta, \cos\theta). \tag{3}$$

The matrix expressing the nutation around the effective field is

$$\mathbf{R}_z(\beta_{\text{eff}}) = \begin{pmatrix} \cos\beta_{\text{eff}} & -\sin\beta_{\text{eff}} & 0 \\ \sin\beta_{\text{eff}} & \cos\beta_{\text{eff}} & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{4}$$

The magnetization (in the tilted frame) after the pulse is

$$\vec{M}'(\tau) = \mathbf{R}_z(\beta_{\text{eff}})\vec{M}'(0) = (\sin\theta\sin\beta_{\text{eff}}, -\sin\theta\cos\beta_{\text{eff}}, \cos\theta). \tag{5}$$

and in the rotating frame (xyz)

$$\begin{aligned} \vec{M}(\tau) &= \mathbf{R}_x(-\theta)\vec{M}'(\tau) \qquad (6) \\ &= (\sin\theta\sin\beta_{\text{eff}}, -\sin\theta\cos\beta_{\text{eff}}\cos\theta + \sin\theta\cos\theta, \sin^2\theta\cos\beta_{\text{eff}} + \cos^2\theta). \end{aligned}$$

c. During the calculation we considered that the norm of the equilibrium magnetization $|\vec{M}(0)|$ is 1, thus the angle α between $\vec{M}(\tau)$ and $\vec{M}(0)$ is simply

$$\alpha = \arccos(\vec{M}(\tau)\vec{M}(0)) = \arccos(\sin^2\theta\cos\beta_{\text{eff}} + \cos^2\theta) \tag{7}$$

We finally get $\alpha = 78.6°$.