The Rotating Frame Approximation

It we work in the rotating frame we can remove the complexity of time-dependence from the problem. The operator that removes the time dependence is:

$$U = exp\{i\omega_{rf} I_z t\}$$

Applying this operator we find

$$\mathcal{H} = -\omega_0 I_z + \omega_1 exp\{i\omega_{rf} I_z t\} \begin{bmatrix} I_x \cos(\omega_{rf} t + \phi) \\ +I_y \sin(\omega_{rf} t + \phi) \end{bmatrix} exp\{-i\omega_{rf} I_z t\}$$

$$+exp\{i\omega_{rf} I_z t\} i\omega_{rf} I_z exp\{-i\omega_{rf} I_z t\}$$

Rotation matrices in NMR

There is a convention regarding directions of rotation that is specific to the experimental geometry that is used in NMR spectrometers. We can write the general rotation operator as:

$$\exp(i\theta I_v) I_u \exp(-i\theta I_v)$$

To yield the following rotation table:

	x	y	z
x	I_x	$I_y \cos(\theta) - I_z \sin(\theta)$	$I_x \cos(\theta) + I_y \sin(\theta)$
y	$I_y \cos(\theta) + I_z \sin(\theta)$	I_y	$I_y \cos(\theta) - I_x \sin(\theta)$
z	$I_z \cos(\theta) - I_y \sin(\theta)$	$I_z \cos(\theta) + I_y \sin(\theta)$	I_z

Properties of Rotations Operators

A key relation used in many of the operator equations is

$$\mathbf{U}\mathrm{f}(\mathbf{A})\mathbf{U}^{-1} = \mathrm{f}(\mathbf{U}\mathbf{f}\mathbf{A}\mathbf{U}^{-1})$$

f(A) is an arbitrary function of operator A. We can expand f(**$\mathbf{UAU^{-1}}$**) as a Taylor series.

$$\mathrm{R}_{\phi}(\alpha,\theta) = \mathrm{R}_{\mathrm{z}}(\phi)\mathrm{R}_{\mathrm{y}}(\theta)\mathrm{R}_{\mathrm{z}}(\alpha)\mathrm{R}_{\mathrm{y}}^{-1}(\theta)\mathrm{R}_{\mathrm{z}}^{-1}(\phi)$$

Properties of Rotations Operators

$$R_\phi(\alpha, \theta) = R_z(\phi)R_y(\theta)R_z(\alpha)R_y^{-1}(\theta)R_z^{-1}(\phi)$$

$$= R_z(\phi)\exp\left[-i\alpha R_y(\theta)I_z R_y^{-1}(\theta)\right]R_z^{-1}(\phi)$$

$$= R_z(\phi)\exp[-i\alpha(I_z \cos\theta + I_x \sin\theta)]R_z^{-1}(\phi)$$

$$= \exp[-i\alpha R_z(\phi)(I_z \cos\theta + I_x \sin\theta)R_z^{-1}(\phi)]$$

$$= \exp\left[-i\alpha(I_z \cos\theta + I_x \cos\phi \sin\theta + I_y \sin\phi \sin\theta)\right]$$

$$= \exp[-i\alpha \mathbf{n} \cdot \mathbf{I}]$$

Rotation Operators in Matrix Form

The operator for a rotation about an arbitrary angle, α, can be represented as a series of rotations about the y and z axes. The five rotations used in this derivation are not independent of one another. The rotation $R_\phi(\alpha,\theta)$ can be reduced to three independent rotations using the Euler method for three dimensional rotation.

$$R_\phi(\alpha) = \begin{bmatrix} \cos\left(\frac{\alpha}{2}\right) & -i\sin\left(\frac{\alpha}{2}\right) e^{-i\phi} \\ -i\sin\left(\frac{\alpha}{2}\right) e^{i\phi} & \cos\left(\frac{\alpha}{2}\right) \end{bmatrix}$$

Rotation Operators in Matrix Form

The angle ϕ determines the axis for rotation perpendicular to the z-axis. $\phi = 0^o$ signifies a rotation about the x axis. The inverse is:

$$\left(R_\phi(\alpha)\right)^{-1} = \begin{bmatrix} \cos\left(\frac{\alpha}{2}\right) & i\sin\left(\frac{\alpha}{2}\right) \\ i\sin\left(\frac{\alpha}{2}\right) & \cos\left(\frac{\alpha}{2}\right) \end{bmatrix}$$

Application to pulsed NMR

The simplest NMR experiment consists of a single pulse followed by aquisition of the FID.

$$R_x(\alpha)I_zR_x^{-1}(\alpha) = \frac{1}{2}\begin{bmatrix} c & -is \\ -is & c \end{bmatrix}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} c & is \\ is & c \end{bmatrix}$$

$$= \frac{1}{2}\begin{bmatrix} c & is \\ -is & -c \end{bmatrix}\begin{bmatrix} c & is \\ is & c \end{bmatrix}$$

$$= \frac{1}{2}\begin{bmatrix} c^2 - s^2 & 2ics \\ -2ics & s^2 - c^2 \end{bmatrix}$$

$$= \frac{1}{2}\begin{bmatrix} \cos\alpha & i\sin\alpha \\ -i\sin\alpha & -\cos\alpha \end{bmatrix}$$

$$= I_z\cos\alpha - I_y\sin\alpha$$

Example of the 180° and 90° Pulse

The Pauli matrices are used here. For example for a 180° pulse we have

$$R_x(\pi)I_zR_x^{-1}(\pi) = \frac{1}{2}\begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} = -\frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = -I_z$$

For a 90° pulse we have

$$R_x(\pi/2)I_zR_x^{-1}(\pi/2) = \frac{1}{2}\begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix} = -\frac{1}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} = -I_y$$

Thus, after a 90° pulse the magnetization will be along $-I_y$. The spins will evolve under the Zeeman Hamiltonian as

$$H_z = (\omega_0 - \omega_{rf})I_z = \Omega I_z$$

Evolution following the 90^o Pulse

We can introduce time-dependence using

$$\sigma(t) = \exp(-iH_z t)\sigma(0)\exp(iH_z t)$$

$$\sigma(t) = \exp(-i\Omega I_z t)\sigma(0)\exp(i\Omega I_z t)$$

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

$$\mathbf{U} = \exp(-i\Omega I_z t) = \begin{bmatrix} \exp(-i\Omega t/2) & 0 \\ 0 & \exp(i\Omega t/2) \end{bmatrix}$$

If we perform the matrix manipulations for $\sigma(0) = -I_y$, we find

$$\sigma(t) = -\frac{1}{2}\begin{bmatrix} \exp(-i\Omega t/2) & 0 \\ 0 & \exp(i\Omega t/2) \end{bmatrix}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\begin{bmatrix} \exp(i\Omega t/2) & 0 \\ 0 & \exp(-i\Omega t/2) \end{bmatrix}$$

Evolution following the 90^o Pulse

$$\sigma(t)$$

$$= -\frac{1}{2}\begin{bmatrix} 0 & -i\exp(-i\Omega t/2) \\ i\exp(i\Omega t/2) & 0 \end{bmatrix}\begin{bmatrix} \exp(i\Omega t/2) & 0 \\ 0 & \exp(-i\Omega t/ \end{bmatrix}$$

$$\sigma(t) = \frac{1}{2}\begin{bmatrix} 0 & i\exp(-i\Omega t) \\ -i\exp(i\Omega t) & 0 \end{bmatrix}$$

$$\sigma(t) = \frac{1}{2}\begin{bmatrix} 0 & i[\cos(\Omega t) - i\sin(\Omega t)] \\ -i[\cos(\Omega t) + i\sin(\Omega t)] & 0 \end{bmatrix}$$

Evolution following the 90^o Pulse

$$\sigma(t) = \frac{1}{2}\begin{bmatrix} 0 & i\cos(\Omega t) + \sin(\Omega t) \\ -i\cos(\Omega t) + \sin(\Omega t) & 0 \end{bmatrix}$$

$$\sigma(t) = \frac{1}{2}\begin{bmatrix} 0 & \sin(\Omega t) \\ \sin(\Omega t) & 0 \end{bmatrix} + \frac{i}{2}\begin{bmatrix} 0 & \cos(\Omega t) \\ -\cos(\Omega t) & 0 \end{bmatrix}$$

$$\sigma(t) = I_x \sin(\Omega t) - I_y \cos(\Omega t)$$

Magnetization with a positive resonance off precesses in the sense x --> y --> -x --> -y.