6. Effective Fields

The introduction of a rotating frame considerably simplifies the motion of nuclear spins in a magnetic field, but it introduces some seemingly unusual effects on the rotation of magnetization vectors by RF fields. The rotating frame of reference is created by removing the radio frequency component of the spins and only observing the audio frequency motion. This is equivalent to the introduction of a fictitious magnetic field, $\mathbf{-\omega/\gamma}$, in addition to the static magnetic field, $\mathbf{B_0}$. The negative sign in front of the fictitious magnetic field indicates that the direction of this field is opposite to that of $\mathbf{B_0}$. If $|\mathbf{-\omega/\gamma}| = |\mathbf{B_0}$, then the total **effective magnetic field** felt by spins of gyromagnetic ratio γ and frequency ω is zero (Figure 6.1a). This means in the presence of the fictitious field, the spins with frequency ω are apparently static. This spin is said to be on-resonance. If the frequency of a spin, I, is not equal to the rotating frame frequency, $-\omega/\gamma$, then the static field is not completely eliminated and a residual field, ΔB, is present (Figure 6.1b). The spin then precesses at a frequency, $\omega_I = \gamma\Delta B$, reflecting the offset from the rotating frame frequency. This spin is off-resonance.

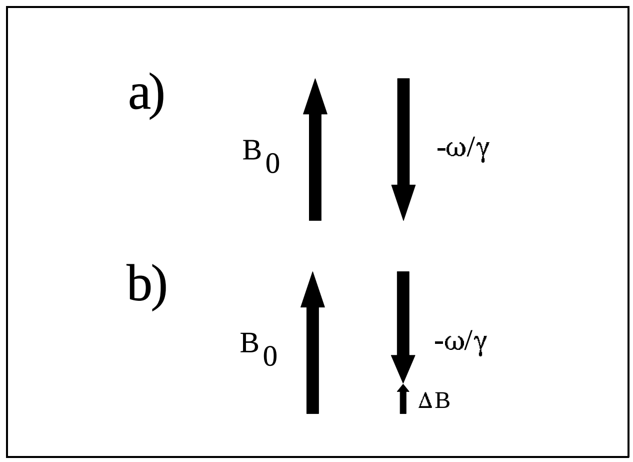

Figure 6.1. Fictitious field, $\mathbf{-\omega/\gamma}$, opposing the static field, $\mathbf{B_0}$. a) If the spin is on resonance, then ΔB=0. b) For spins not on resonance then there is a residual field, ΔB.

In all of our discussions, unless qualified, an implicit assumption is that the spin has been transformed to the rotating frame. In the product operator formalism, rotations about the Z axis are used to describe the precession of spins in the rotating frame. For example, a spin that is along the X axis would rotate toward the Y axis as:

$$\mathbf{I_x} \; =\omega_I t\hat{\mathbf{I}}_z\!\!=\!\!> \mathbf{I_x} \cos \omega_I t + \mathbf{I_y} \sin \omega_I t$$

The precession angle is given as the product of the frequency, ω_I, and the time of precession, t. Obviously, if the spin is on-resonance then $\omega_I = 0$ and there is no apparent motion of the spin vector.

Excitation in NMR is accomplished by applying a RF field with a frequency near the resonance frequency of the spin system. Commonly, the frequency of the applied RF field is chosen as the rotating frame frequency. Any oscillating electromagnetic field produces both an electric and a magnetic field. We will disregard the electric component since it does not interact with nuclear spins. The oscillating magnetic field, $\cos(\omega_{RF})$, can be described by the sum of two rotating components with opposite directions. A famous formula of Euler is:

$$\cos(x) = 1/2*(e^{ix} + e^{-ix})$$

We will use this relationship later, but for now suffice it to say that the functions $e^{\pm ix}$ represent magnetization vectors that rotate about the Z axis in the XY plane. The sign of the argument describes the direction of the rotation. In NMR only the magnetic component that is traveling in the same direction as the precessing nuclear spins has any significant interaction with the system. In a reference frame that is rotating at the frequency of the RF magnetic field component, the magnetization vector appears static. We can describe the applied RF field as a static magnetic field applied to the spins.

The magnetic field experienced by the nuclear spins is the vector sum of all of the applied fields (Figure 6.2). For a spin that is off-resonance by an amount **ΔB** and subjected to a RF magnetic field of $\mathbf{B_1}$, The spin will precess around the vector sum of the fields, $\mathbf{B_{eff}}$. If $\Delta B = 0$, then precession of the spin is about the applied RF field. If the RF magnetic component is along the X axis in the rotating frame of reference, then the on-resonance spin, initially along the Z axis, will precess around the X axis in the YZ plane at a frequency $\gamma\mathbf{B_{eff}} = \gamma\mathbf{B_1}$. In product operators:

$$\mathbf{I_z} \xrightarrow{\theta\hat{\mathbf{I}}_x} \mathbf{I_z}\cos\theta - \mathbf{I_y}\sin\theta$$

Notice the direction of rotation (by convention) is from the Z axis toward the Y axis.

If, however, the frequency of the spin is not equal to the rotating frame frequency, which is equal to the RF field frequency, then there is a residual field along the Z axis (the direction of the static field), $\mathbf{\Delta B} \neq 0$. The effective field, which is the axis that the spins will precess about, no longer lies in the XY axis but is tilted toward the Z axis by an angle:

$$\phi = \mathrm{ARCTAN}\ (\mathbf{\Delta B}/\mathbf{B_1})$$

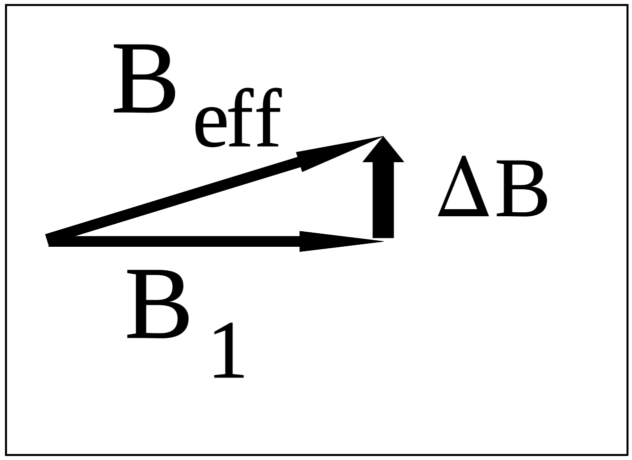

Figure 6.2. Vector addition of the residual static field, **ΔB**, and the applied RF magnetic field, $\mathbf{B_1}$, to give an effective field, $\mathbf{B_{eff}}$.

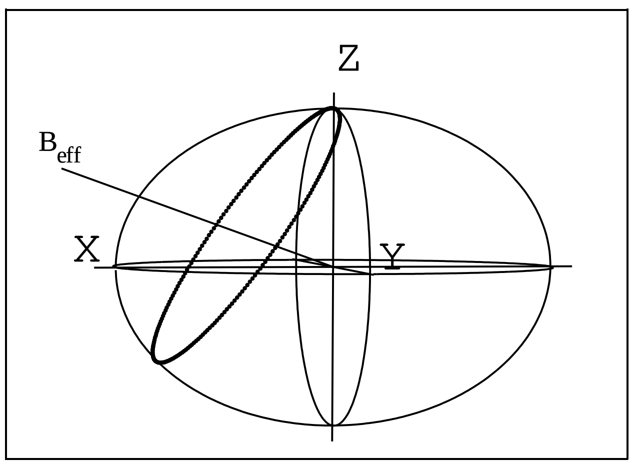

Figure 6.3. Trajectory of tip of a spin vector around a tilted $\mathbf{B_{eff}}$.

and the magnitude of the effective field is (Figure 6.3):

$$|\mathbf{B_{eff}}| = (|\mathbf{B_1}|^2 + |\Delta\mathbf{B}|^2)^{1/2}$$

Several immediate consequences can be drawn from this analysis:

1. If $\mathbf{B_1} \gg \Delta\mathbf{B}$ then the angle ϕ is close to 0° and the spins will precess about the $\mathbf{B_1}$ field in the XY plane.

2. If $\mathbf{B_1} \ll \Delta\mathbf{B}$ then the angle ϕ is close to 90° and the spins will precess about the $\Delta\mathbf{B}$ (or the Z) axis field in the XY plane. This is the case when there is no applied RF field, $\mathbf{B_1} = 0$.

3. If the spin is off-resonance, then the magnitude of the rotating field is larger than the applied field. For example, assume that $\mathbf{B_1}$ applied for a time, t, causes a spin to precess 2π radian (360°): $2\pi = \gamma\mathbf{B_1}t$. If a spin is off-resonance by a frequency, $\gamma\mathbf{B_1}$, then $B_{eff} = (2*\gamma\mathbf{B_1}^2)^{1/2}$. The effective field is $\sqrt{2} \approx 1.4$ times as strong as the applied RF field. The off-resonance spin will precess $\sqrt{2}*\gamma\mathbf{B_1}t$ or $\sqrt{2}*2\pi$ radian = (509°).

4. The precession axis for an off-resonance spin no longer lies in the XY plane. A rotation of π/2 around a tilted axis can not rotate a spin initially along the Z axis into the XY plane. In fact, if the spin is far enough off resonance, the spin can never reach the XY plane.

The calculation of the trajectory of a spin around a tilted axis as in the case of an off-resonance spin is slightly more complicated that a rotation around the X or Y axis. Figure 6.4 shows the sequence of rotations required to rotate a vector around an axis that is no along the X, Y or Z.
Specifically, Figure 6.4 illustrates a rotation of $\mathbf{I_z}$ magnetization around an axis that is tilted away from the Y axis toward the Z axis by an off-resonance effect. We can't directly rotate the vector around the tilted axis because the rotations that we have are only defined if the rotation axis is along one of the principle axes (these rotations can be easily obtained by matrix multiplication). It is apparent that the magnetization vector is less than 90° away from the rotation axis (Figure 6.4a). If we rotate the magnetization toward the Y axis until

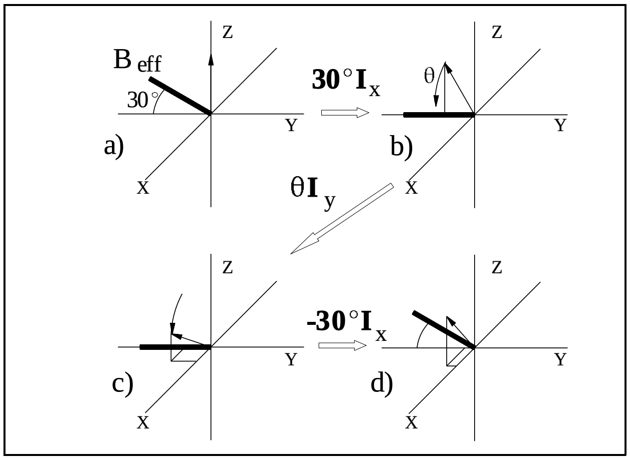

Figure 6.4. Rotation of $\mathbf{I_z}$ magnetization about a tilted effective field, $\mathbf{B_{eff}}$.

the vector lies at the same angle away from the Y axis as it does from the original rotation axis (Figure 6.4b), then we can use the rotation operator about the Y axis that we already have (Figure 6.4c). Subsequently, after the rotation about the Y axis, we must return the magnetization back toward the Z axis by a rotation that is opposite and equal two the first rotation (Figure 6.4d). To make this a bit more concrete, assume that, as in Figure 6.4, an off-resonance spin is subjected to a rotation by RF field along the Y axis that causes the effective field to be 30° away from the Y axis and causes an on-resonance spin to traverse an angle of θ about the Y axis. The rotations required for this transformation are:

$=30°\hat{\mathbf{I}}_x\Rightarrow \ =\theta_{eff}\hat{\mathbf{I}}_y\Rightarrow \ =-30°\hat{\mathbf{I}}_x\Rightarrow$

The first operation is to rotate the magnetization around the X axis until the effective field lies along the Y axis.

$\mathbf{I}_z \ =30°\hat{\mathbf{I}}_x\Rightarrow \mathbf{I}_z \cos 30° - \mathbf{I}_y \sin 30°$

Next we rotate around the "new" Y axis by an angle θ_{eff}. By simple trigonometry, the strength of the effective magnetic field is given by:

$\mathbf{B}_{eff} = \mathbf{B}_1/\mathrm{COS}(30°)$

Thus the effective rotation angle, θ_{eff}, will be θ/COS(30°). If we now assume that the rotation angle, θ, is 90°, then θ_{eff} = 90°/COS(30°) = 103.92°. The rotation around the Y axis yields:

$$\mathbf{I}_z \cos 30° - \mathbf{I}_y \sin 30° \ =103.92°\hat{\mathbf{I}}_y\Rightarrow (\mathbf{I}_z \cos 103.92° + \mathbf{I}_x \sin 103.92°) \cos 30° - \mathbf{I}_y \sin 30°$$

Finally, the magnetization is returned by a -30° X axis rotation,

$$(\mathbf{I}_z \cos 103.92° + \mathbf{I}_x \sin 103.92°) \cos 30° - \mathbf{I}_y \sin 30°$$

$$=-30°\hat{\mathbf{I}}_x\Rightarrow$$

$$(\mathbf{I}_z \cos -30° - \mathbf{I}_y \sin -30°) \cos 103.92° \cos 30° + \mathbf{I}_x \sin 103.92° \cos 30° - (\mathbf{I}_y \cos -30° + \mathbf{I}_z \sin -30°) \sin 30°$$

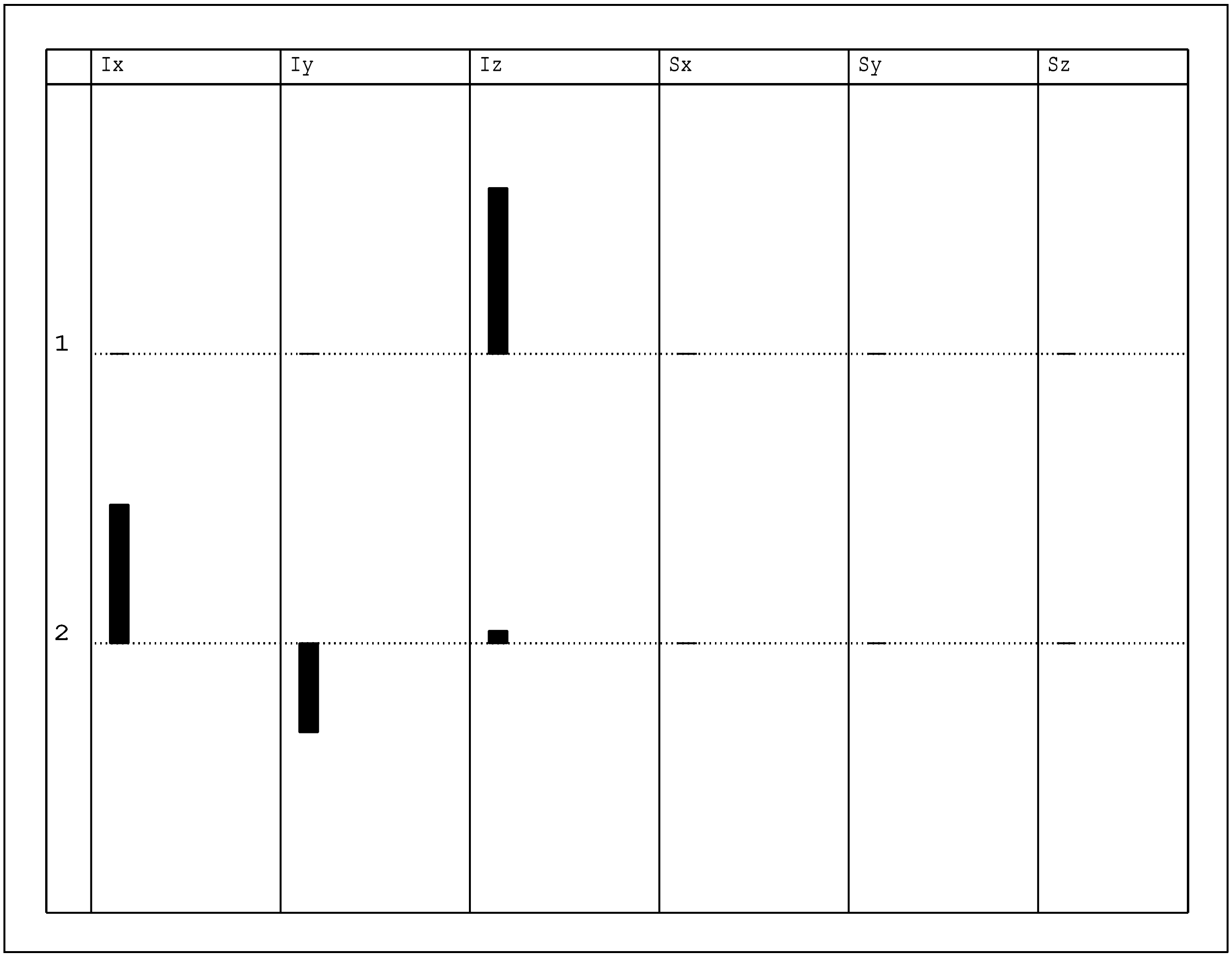

Figure 6.5. Histogram representing a θ_{eff} = 103.92° rotation about an axis tilted 30° from the Y axis.

Collecting terms, the final result is:

$\mathbf{I_z}$ * cos -30° * cos 103.92° * cos 30° - sin -30° * sin 30° = 0.07 * $\mathbf{I_z}$

+ $\mathbf{I_x}$ sin 103.92° * cos 30° = 0.841 * $\mathbf{I_x}$

- $\mathbf{I_y}$ (sin -30° * cos 103.92° * cos 30° + cos -30° * sin 30°) = -0.537 * $\mathbf{I_y}$

Figure 6.5 shows the histogram for this rotation.

Phase Shifted Rf Pulses

This method of rotating vectors about axis that do not lie along one of the principle axis is also used to generate phase shifts about the Z axis. For example:

$\mathbf{I_z}$ $=\pi/2\hat{\mathbf{I}}_{45^\circ}$=> ?

is an example of a 90° rotation of a vector, $\mathbf{I_z}$, about an axis that is shifted by 45° from the X axis. The sequence can be rewritten as:

$\mathbf{I_z}$ $=45^\circ\hat{\mathbf{I}}_z$=> $=\pi/2\hat{\mathbf{I}}_y$=> $=-45^\circ\hat{\mathbf{I}}_z$=>

The sequence rotates state vector by 45° to align it with the rotation axis, followed by the π/2 rotation about the X axis, and then rotates the magnetization back to its original position. Notice that from a vector lying along the Z axis, the first rotation does nothing, but if the magnetization is in the XY plane then there is a rotation (Figure 6.6).

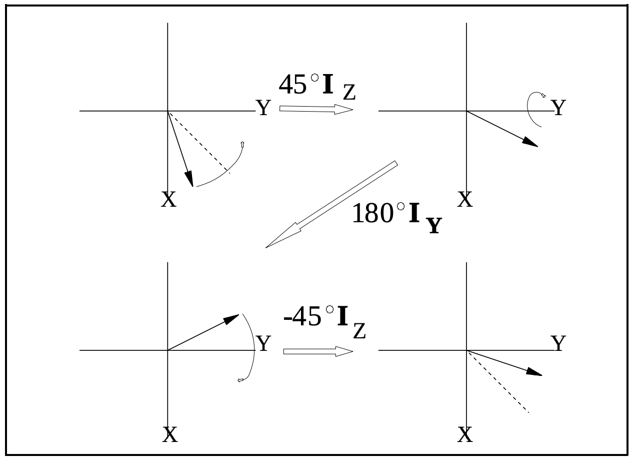

Figure 6.6 180° rotation of a vector in the XY plane about an axis phase shifted 45° away from the X axis.