### 3.1 Rotational frequencies and angles

Rotations about an axis take a finite amount of time. The time for a vector to rotate 360° (2π radian) is the "period" with units of seconds/cycle (1/Hertz). The reciprocal of the period is the "frequency" and has units of cycles/second or Hertz. No matter what physical property causes a rotation of the magnetization vector (radiofrequency pulse, chemical shift, coupling) there is an associated frequency. The angle subtended by a vector with an angular velocity of ω (2πν) in a period of time t is ω*t (2πν*t).

| | |
|---|---|
| Frequency | Hertz(cycles/second)<br>2πν<br><br>radian/sec<br>ω |
| Angle (Frequency* time) | Hz*t = 2πν*t<br><br>(Rad/s)*t = ω*t |

*In NMR spectroscopy the signal that is detected is proportional to the projection of the magnetization vector onto the XY plane (a*$I_x$, b*$I_y$).* If the magnetization is aligned along the +Z or -Z axis then there is a zero projection in the XY plane and there is no detectable signal. If the magnetization lies perpendicular to the Z axis (i.e. in the XY plane) then the signal strength is at a maximum. The XY projection of a magnetization vector that has an angle of ϕ away from the Z axis can be easily calculated using trigonometry.

One important point worth mentioning here is that *the only directly observable quantities of any spin system are the components of the magnetization vector that lie in the XY plane (**$I_x$** or **$I_y$**).* This becomes very important to remember in the coupled spin systems that we will encounter later. Magnetization along the Z axis can be directly observed with special experiments and hardware that will not be discussed.

### 3.2 Right-handed Cartesian coordinates

positive rotation about Y:
Z → X → -Z → -X → Z

positive rotation about X:
Z → -Y → -Z → Y → Z

positive rotation about Z:
X → Y → -X → -Y → X

The X,Y,Z coordinates of can be arranged in two orientations, right- and left-handed. In order to retain consistency, all of the coordinate axes and rotations we use here will be right-handed. A right-handed coordinate system is such that if one curls the fingers of the right hand, the fingers will travel from the X axis to the Y axis and the thumb will point along the Z axis. Mathematically, the cross product (⊗) of the unit vectors X ⊗ Y results in a vector aligned along the positive Z axis. In this system, a positive rotation of a Z vector about the Y axis will carry the vector towards the positive X axis.

Note that this convention is not universal. Many NMR texts rotate the vector in the opposite direction ( *e.g.* van de Ven,1995). The convention used here is that used by Ernst et al in *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*. The general convention is that for a RF magnetic field applied along the negative X (or Y) axis the rotation vector for a nucleus with a positive gyromagnetic ratio lies along the Positive X (or Y) axis. For rotations around the Z axis, it is assumed that for a positive rotation (X → Y → -X → -Y) the carrier frequency is placed above the resonance frequency, that is, $\omega_{RF} > \omega_0$.

*In all rotations of the state vector, only components that are orthogonal (at right angles to) the axis of rotation are effected.* In a simplified treatment of NMR spectroscopy that neglects the effects of being "off-resonance" (we will consider this later) the rotation axes for all interactions lie either along the Z (longitudinal) axis or somewhere in the X, Y (transverse) plane. Rotations about the Z axis are due to chemical shifts or phase shifts. Rotations about axes in the XY plane are RF pulses.

If a Z vector representing the **I** magnetization, (0*$\mathbf{I}_x$, 0*$\mathbf{I}_y$, 1*$\mathbf{I}_z$) or ($\mathbf{I}_z$), is rotated about the X axis by 90° (π/2 radian), the vector will then lie along the -Y axis ($\mathbf{I}_y$) (Figure 3.1). If the rotation angle is increased to 180° (π radian), then **I** it will rotate to the -Z axis (-$\mathbf{I}_z$). Obviously, a 2π rotation will return the vector to the Z axis ($\mathbf{I}_z$). The direction of rotation is given by a cross product of X ⊗ Z, that is, Y = X ⊗ Z. The result of a 90° pulse along the X axis will rotate a vector initially along the Z axis towards the Y axis.

A rotation by π/2 about the X axis of a vector initially along the Z axis will be designated as:

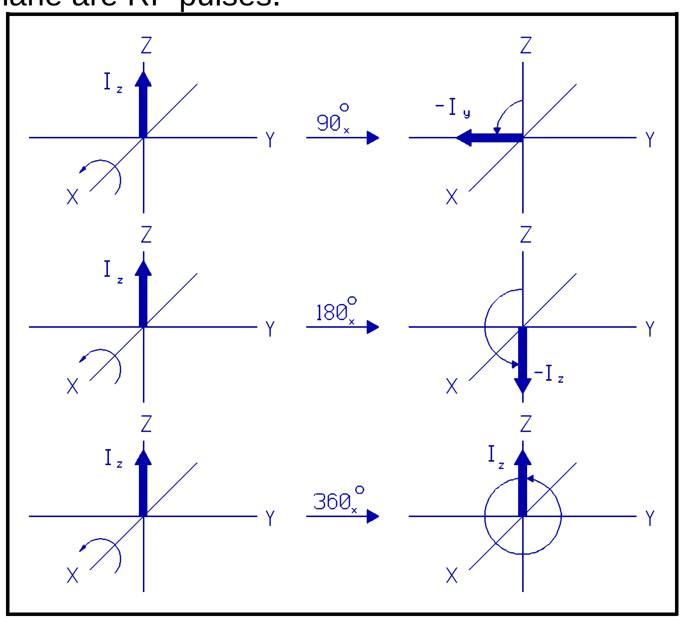



**Figure 3.1.** Rotations of **I** by 90°, 180°, and 360° around the X axis.

$\mathbf{I}_z$ =π/2$\hat{\mathbf{I}}_x$=> -$\mathbf{I}_y$

This represents $\mathbf{I}_z$ magnetization being tipped by 90° (π/2 radian) around the X axis to -$\mathbf{I}_y$ (this is a positive rotation). A smaller rotation of say 45° about the X axis would leave the vector somewhere in the YZ plane between the Z axis and the -Y axis. To put this on a more quantitative basis we can resort to trigonometry.  Figure 3.2 shows the trigonometric relationships of the components of a vector that is tilted away from the Z axis toward the Y axis by 45° (π/4).  The Z component is equal to cos(45°) and the Y component, $-\mathbf{I}_y$, is equal to sin(45°).

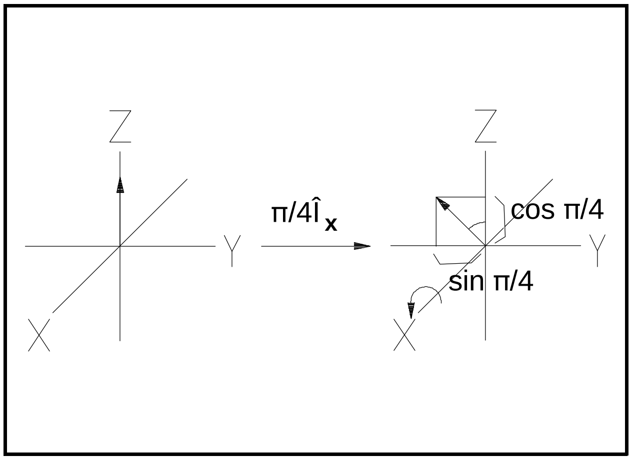



**Figure 3.2.** Components of a vector initially along the Z axis rotated about the X axis by the angle π/4 (45°). The  (-)Y component is sin π/4 and the Z component is cos π/4.

In the notation that we will be using to describe rotations such as this, a 45° (π/4) rotation about the X axis of a vector initially along the Z axis, $\mathbf{I}_z$, will be represented as:

$\mathbf{I}_z \; =\pi/4\hat{\mathbf{I}}_x \Rightarrow \mathbf{I}_z \cos \pi/4 - \mathbf{I}_y \sin \pi/4$

Note that the rotation is positive, that is, the Z component rotates toward the Y axis with a positive rotation about the X axis. For the general rotation, θ:

$\mathbf{I}_z \; =\theta\hat{\mathbf{I}}_x \Rightarrow \mathbf{I}_z \cos \theta - \mathbf{I}_y \sin \theta$

Note that when θ is greater than π (180°), sin θ < 0.  If θ is 270° (3π/2), sin 3π/2 = -1 and the final position for the vector is along the positive Y axis.

$\mathbf{I}_z \; =3\pi/2\hat{\mathbf{I}}_x \Rightarrow \mathbf{I}_z \cos 3\pi/2 - \mathbf{I}_y \sin 3\pi/2$

$\equiv \; \mathbf{I}_z * 0 - \mathbf{I}_y * -1$

$\equiv \; \mathbf{I}_y$

The same result would be obtained by rotating the vector in a negative direction about the same axis:

$\mathbf{I}_z \; =-\pi/2\hat{\mathbf{I}}_x \Rightarrow \mathbf{I}_y$

Vector rotations in 3 dimensions can be determined by following simple rules.

1) Rotate each component of the vector independently.
2) Obtain the result by multiplying the initial vector by cos(arg) and adding sin(arg) times the vector obtained by the cross product of the rotation axis into the initial vector, which is obtained from the right hand rule of turning the rotation axis into the initial vector axis with the thumb pointing toward the

final axis.

The argument of the sine and cosine functions is the angle of rotation.  As an example, use the following sequence:

$\mathbf{I}_z$ =$\theta\hat{\mathbf{I}}_x$=> ?  =$\beta\hat{\mathbf{I}}_y$=> ?  =$\omega_I t\hat{\mathbf{I}}_z$=> ?

This sequence would be diagrammed as:

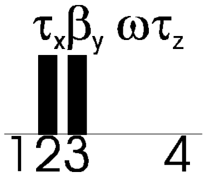



Figure 3.3 represents the motion of a 3 dimensional vector initially along the Z axis ( $\mathbf{I}_z$ ) subjected to this series of rotations.

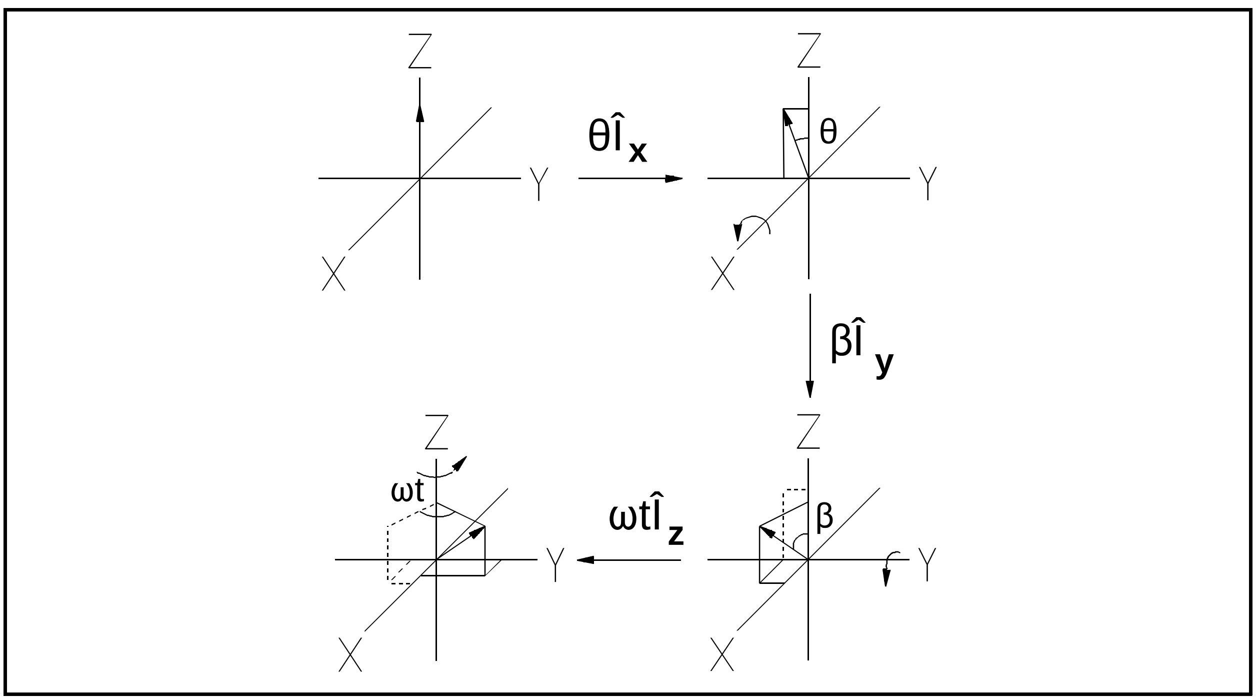



**Figure 3.3.** Vector representation of a sequence of rotations.
( =$\theta\hat{\mathbf{I}}_x$=>  =$\beta\hat{\mathbf{I}}_y$=>  =$\omega_I t\hat{\mathbf{I}}_z$=> )

Starting with the vector $\mathbf{I}_z$, rotate it around the X axis by an angle θ.
Using the right hand rule, moving the rotation axis, X, into the initial axis, Z, points the thumb toward the negative Y axis.  The rotation angle is θ, so $\mathbf{I}_z$, the initial vector, is multiplied by cos(θ) and the final axis, $-\mathbf{I}_y$, is multiplied by sin(θ).

$\mathbf{I}_z \xrightarrow{\theta \hat{I}_x} \mathbf{I}_z \cos\theta - \mathbf{I}_y \sin\theta$

Continuing with the next rotation of β about $\mathbf{I}_y$:

$$\mathbf{I}_z \cos\theta - \mathbf{I}_y \sin\theta \xrightarrow{\beta \hat{I}_y} (\mathbf{I}_z \cos\beta + \mathbf{I}_x \sin\beta) \cos\theta - \mathbf{I}_y \sin\theta$$

$$\equiv \mathbf{I}_z \cos\beta \cos\theta + \mathbf{I}_x \sin\beta \cos\theta - \mathbf{I}_y \sin\theta$$

Each of the components, $\mathbf{I}_z$ and $\mathbf{I}_y$, are treated independently. The rotation about the Y axis carries the $\mathbf{I}_z$ component towards the $\mathbf{I}_x$ axis with the appropriate cosine and sine multipliers. *The $\mathbf{I}_y$ component is not effected by a rotation about the parallel Y axis* (Figure 3.4). Notice that the components retain the multipliers that were gained during the first rotation.

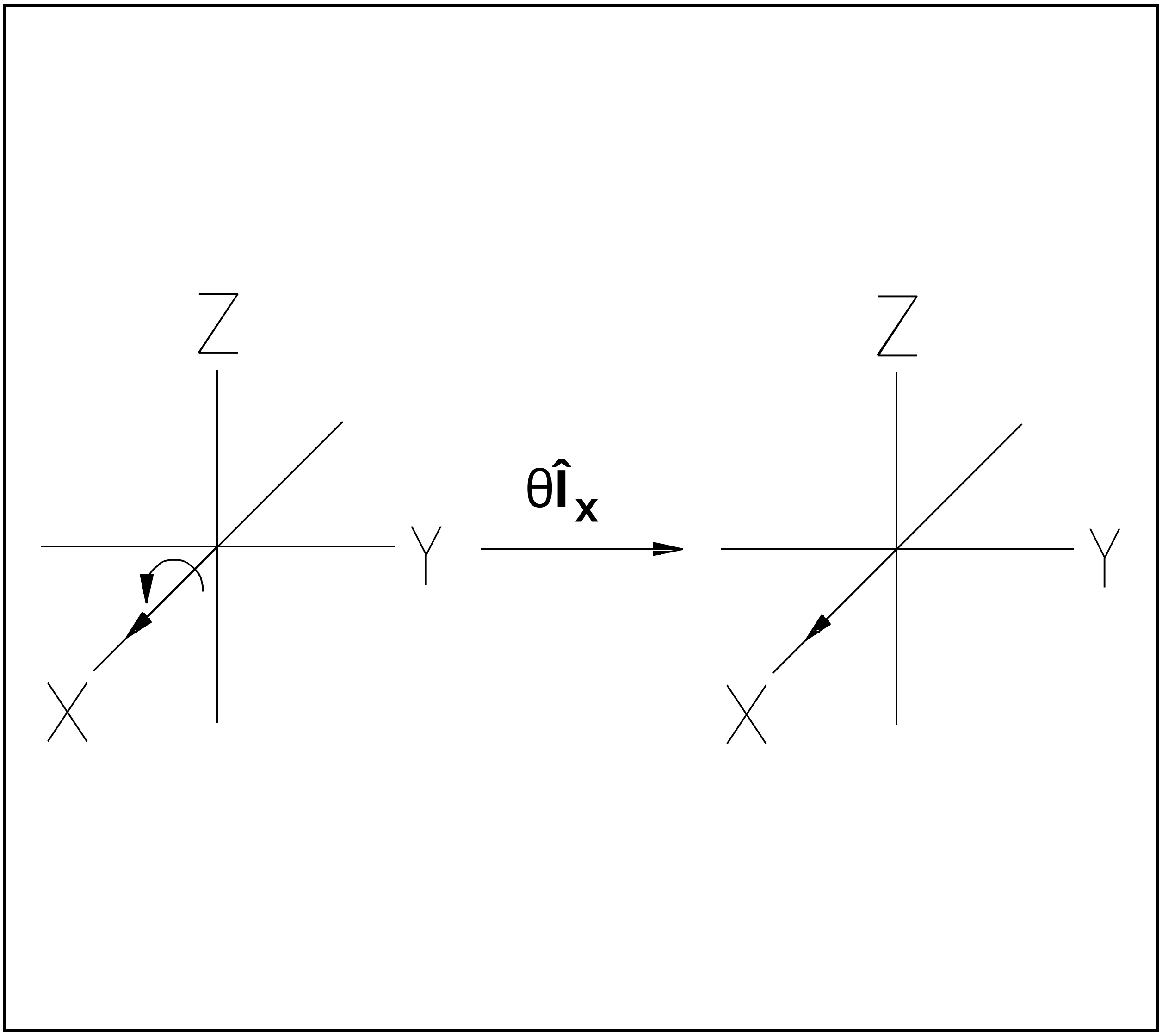



**Figure 3.4** Vectors that are collinear with the rotation axis are invariant to the rotation. ($\mathbf{I}_x \overset{\theta \hat{\mathbf{I}}_x}{=\!\!>} \mathbf{I}_x$)

The final rotation is calculated as:

$$\begin{aligned}&\mathbf{I}_z \cos\beta \cos\theta && && \mathbf{I}_z \cos\beta \cos\theta \\ &+ \mathbf{I}_x \sin\beta \cos\theta && =\omega_I t \hat{\mathbf{I}}_z => && + (\mathbf{I}_x \cos\omega_I t + \mathbf{I}_y \sin\omega_I t) \sin\beta \cos\theta \\ &- \mathbf{I}_y \sin\theta && && - (\mathbf{I}_y \cos\omega_I t - \mathbf{I}_x \sin\omega_I t) \sin\theta\end{aligned}$$

$$\begin{aligned}\equiv\ &\mathbf{I}_z \cos\beta \cos\theta \\ &+ \mathbf{I}_x (\cos\omega_I t \sin\beta \cos\theta + \sin\omega_I t \sin\theta) \\ &+ \mathbf{I}_y (\sin\omega_I t \sin\beta \cos\theta - \cos\omega_I t \sin\theta)\end{aligned}$$

In calculating these rotations, it becomes obvious that it one can quickly become mired in a huge pile of trig functions and spin operators which degrades the simplicity of this formalism. The use of a computer can eliminate the difficulty at the expense of loss of understanding. The best approach is to introduce simplifications that do not compromise accuracy, but retain the overall understanding of a sequence of rotations. However, at times it is necessary to "bite the bullet" and just do the entire calculation.

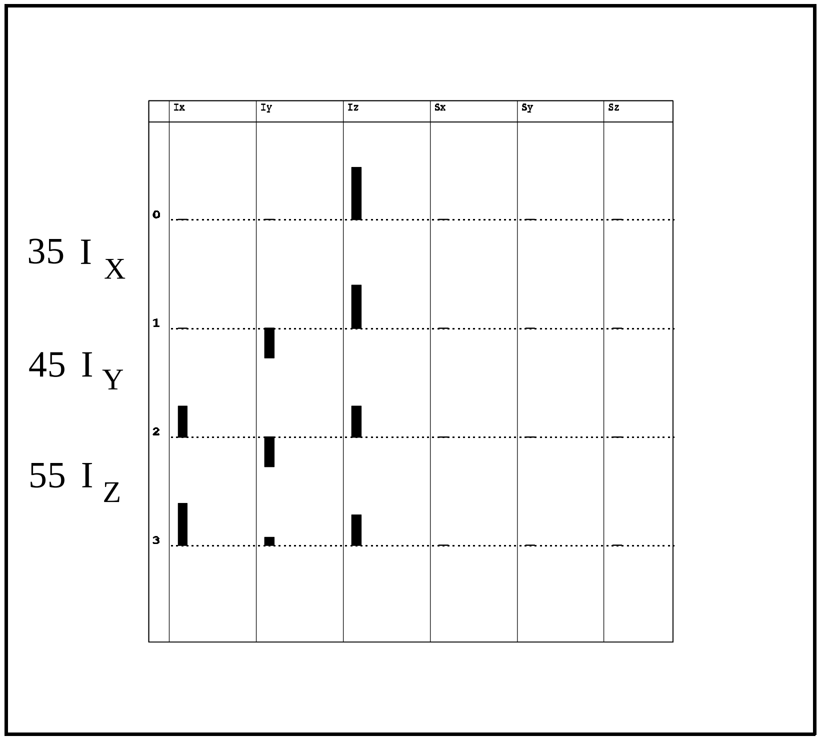



**Figure 3.5.** Histogram for the sequence:
$\mathbf{I_z}$ = **35**° $\hat{\mathbf{I}}_x$=> =**45**° $\hat{\mathbf{I}}_x$=> =**55**° $\hat{\mathbf{I}}_z$=>.

Computers can certainly simplify the calculation of complicated sequences, but this approach tends to hide the understanding in a black-box. Figure 3.5 is a histogram created from a computer simulation of the motion of the state vector during the pulse sequence:

$\mathbf{I_z}$ =$\theta\hat{\mathbf{I}}_x$=> ? =$\beta\hat{\mathbf{I}}_y$=> ? =$\omega_I t\hat{\mathbf{I}}_z$=> ?

With the angles: θ = 35°, β = 45°, and $\omega_I t$ = 55°. The numbered steps in the histogram refer to positions in the pulse sequence.

As an example of how proper choices of rotation variables can simplify the calculations consider the sequence:

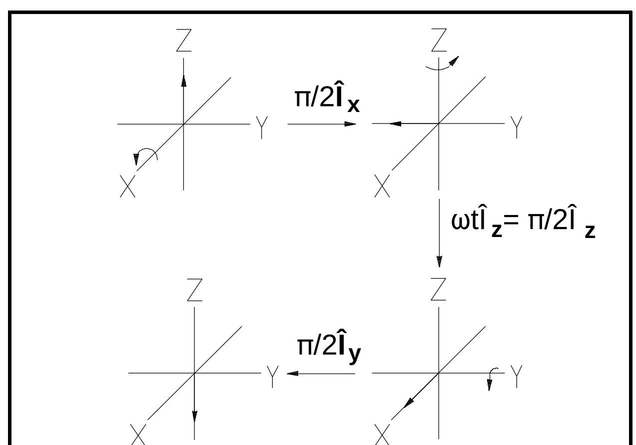
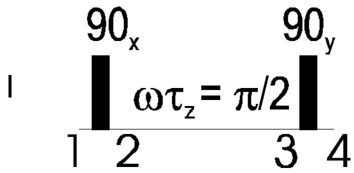



**Figure 3.6.** Vector diagram for the pulse sequence:
$\mathbf{I_z}$ =$\pi/2\hat{\mathbf{I}}_x$=> =$\pi/2\hat{\mathbf{I}}_z$=> =$\pi/2\hat{\mathbf{I}}_y$=>




The vector motion is shown in Figure 3.6 and the corresponding histogram is shown in Figure 3.7.

The sequence is calculated as above but with the substitutions of particular rotation angles.

$\mathbf{I}_z \; =\pi/2\hat{\mathbf{I}}_x\!\!=> -\mathbf{I}_y \; =\pi/2\hat{\mathbf{I}}_z\!\!=> \mathbf{I}_x \; =\pi/2\hat{\mathbf{I}}_y\!\!=> -\mathbf{I}_z$

Compare this to the general calculation:

$\mathbf{I}_z \quad =\theta\hat{\mathbf{I}}_x\!\!=> \quad \mathbf{I}_z \cos\theta - \mathbf{I}_y \sin\theta$

$=\omega_I t\hat{\mathbf{I}}_z\!\!=> \quad \mathbf{I}_z \cos\theta - (\mathbf{I}_y \cos\omega_I t - \mathbf{I}_x \sin\omega_I t)\sin\theta$

$=\beta\hat{\mathbf{I}}_y\!\!=> \quad (\mathbf{I}_z \cos\beta + \mathbf{I}_x \sin\beta)\cos\theta - \mathbf{I}_y \cos\omega_I t \sin\theta$
$+ (\mathbf{I}_x \cos\beta - \mathbf{I}_z \sin\beta)\sin\omega_I t \sin\theta$

$\equiv \quad + \mathbf{I}_z (\cos\beta\cos\theta - \sin\beta\sin\omega_I t\sin\theta)$
$- \mathbf{I}_y \cos\omega_I t \sin\theta$
$+ \mathbf{I}_x (\sin\beta\cos\theta + \cos\beta\sin\omega_I t\sin\theta)$

Upon substituting cos π/2=0 and sin π/2=1,

$\equiv \; \mathbf{I}_z * (-1) = -\mathbf{I}_z$

is obtained.  This is just to point out that when there are substitutions that make life simpler, you should take advantage of them.

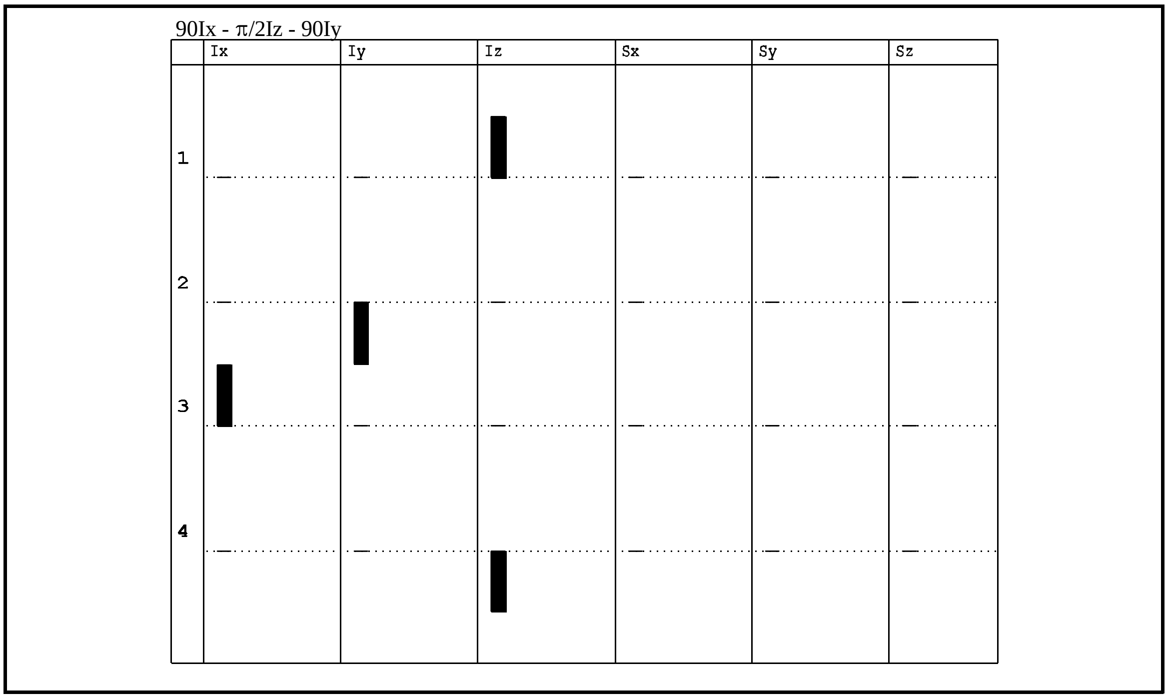



**Figure 3.7** Histogram for sequence: $=\pi/2\hat{\mathbf{I}}_x \Rightarrow \; =\omega_I t\hat{\mathbf{I}}_z \Rightarrow \; =\pi/2\hat{\mathbf{I}}_y \Rightarrow$