4.1 Rotation Matrices

The mathematics of vector rotations is the realm of matrix algebra. All rotations can be described by the multiplication of matrices. Although we will not use matrix multiplications very often in describing the rotations of NMR, the methods will serve as a useful model to introduce and visualize some rather bizarre ideas that we will encounter in coupled spin systems. Matrix methods are also very easy to program on a computer and can be of great assistance in analyzing complicated pulse sequences.

$$\underset{\textit{Rotation matrix}}{\underset{\phi^{I}\hat{I}_x \atop \Rightarrow}{\begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\phi & -\sin\phi \\ 0 & \sin\phi & \cos\phi \end{bmatrix}}} \; \underset{\textit{Vector}}{\underset{I}{\begin{bmatrix} a * \mathrm{I_x} \\ b * \mathrm{I_y} \\ c * \mathrm{I_z} \end{bmatrix}}} \tag{1}$$

This is the matrix representation for a rotation. The one shown is for a rotation of an angle ϕ about the x axis. The matrix with 3 rows and 3 columns (3 X 3) is the rotation matrix and it "operates" on the 3 X 1 vector matrix which represents the magnetization vector.

To multiply a matrix and a vector, first the top row of the matrix is multiplied element by element with the column vector, then the sum of the products becomes the top element in the resultant vector. The next row times the column vector gives the middle element of the resultant and likewise for the third.

$$\begin{bmatrix} a & b & c \\ d & e & f \\ g & h & i \end{bmatrix} \begin{bmatrix} \mathrm{I_x} \\ \mathrm{I_y} \\ \mathrm{I_z} \end{bmatrix} = \begin{bmatrix} a * \mathrm{I_x} + b * \mathrm{I_y} + c * \mathrm{I_z} \\ d * \mathrm{I_x} + e * \mathrm{I_y} + f * \mathrm{I_z} \\ g * \mathrm{I_x} + h * \mathrm{I_y} + i * \mathrm{I_z} \end{bmatrix} \tag{2}$$

If a vector, **I**, has the components [$0*I_x$,$0*I_y$,$1*I_z$] or $\mathbf{I_z}$, then the a rotation of 90° $\mathbf{I_x}$ (π/2 radian) be represented as:

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos(90^\circ) & -\sin(90^\circ) \\ 0 & \sin(90^\circ) & \cos(90^\circ) \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} = \begin{bmatrix} ? \\ ? \\ ? \end{bmatrix} \tag{3}$$

$$\left(\underset{\Rightarrow}{90^\circ} \hat{I}_x \right) \qquad (I_z) =$$

which since cos(90°) = 0 and sin(90°) = 1 gives:

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 0 \\ -1 \\ 0 \end{bmatrix} \tag{4}$$

The resulting vector is [0*$\mathbf{I}_x$,-1*$\mathbf{I}_y$,0*$\mathbf{I}_z$] or -$\mathbf{I}_y$. In standard product operator notation,

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

The rotation matrices for rotations of a three dimensional vector around the three coordinate axes are:

$$\underset{\underset{\Rightarrow}{\phi^I\hat{I}_x}}{\begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\phi & -\sin\phi \\ 0 & \sin\phi & \cos\phi \end{bmatrix}} \quad \underset{\underset{\Rightarrow}{\phi^I\hat{I}_y}}{\begin{bmatrix} \cos\phi & 0 & \sin\phi \\ 0 & 1 & 0 \\ -\sin\phi & 0 & \cos\phi \end{bmatrix}} \quad \underset{\underset{\Rightarrow}{\omega^I\hat{I}_z}}{\begin{bmatrix} \cos\omega & -\sin\omega & 0 \\ \sin\omega & \cos\omega & 0 \\ 0 & 0 & 1 \end{bmatrix}} \qquad \textbf{(5)}$$

In most sequences there are more than one rotation. As an example, consider a sequence that rotates $\mathbf{I_z}$ by 90° about the X axis followed by a rotation of ωt about the Z axis. In standard notation:

$$\mathbf{I_z} \; =\pi/2\hat{\mathbf{I}}_\mathbf{x}\!=\!> \; =\omega_\mathrm{I} t\hat{\mathbf{I}}_\mathbf{z}\!=\!> ?$$

In matrix notation:

$$\underset{\underset{\Rightarrow}{\omega^I\hat{I}_z}}{\begin{bmatrix} \cos\omega^I t & -\sin\omega^I t & 0 \\ \sin\omega^I t & \cos\omega^I t & 0 \\ 0 & 0 & 1 \end{bmatrix}} * \underset{\underset{\Rightarrow}{\phi^I\hat{I}_x}}{\begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos 90^\circ & -\sin 90^\circ \\ 0 & \sin 90^\circ & \cos 90^\circ \end{bmatrix}} * \underset{\mathrm{I_z}}{\begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}} = \begin{bmatrix} ? \\ ? \\ ? \end{bmatrix} \qquad \textbf{(6)}$$

Note that the order of time sequential matrices is from right to left. The first rotation is next to the vector and the next rotation is placed to the left. The order of rotations is very important. Once the physical order of matrices is established, the order of multiplication is irrelevant. The rightmost matrix can multiply the vector yielding a resultant vector which is then multiplied by the next matrix to give the final vector. Alternatively, the two matrices can be multiplied together first and then the resultant matrix can multiply the vector. Both results will be the same. However, transposing the matricies will, in general, completely change the outcome. To multiply two matrices together:

$$\begin{bmatrix} a & b & c \\ d & e & f \\ g & h & i \end{bmatrix} * \begin{bmatrix} A & B & C \\ D & E & F \\ G & H & I \end{bmatrix} = \begin{bmatrix} aA+bD+cG & aB+bE+cH & aC+bF+cI \\ dA+eD+fG & dB+eE+fH & dC+eF+fI \\ gA+hD+iG & gB+hE+iH & gC+hF+iI \end{bmatrix} \qquad \textbf{(7)}$$

Using Equation 7 we can calculate the overall rotation of the sequence.

$$\begin{bmatrix} \cos\omega_l t & -\sin\omega_l t & 0 \\ \sin\omega_l t & \cos\omega_l t & 0 \\ 0 & 0 & 1 \end{bmatrix} * \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos 90^\circ & -\sin 90^\circ \\ 0 & \sin 90^\circ & \cos 90^\circ \end{bmatrix} * \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} = \begin{bmatrix} ? \\ ? \\ ? \end{bmatrix}$$

$$\begin{bmatrix} \cos\omega_l t & -\sin\omega_l t & 0 \\ \sin\omega_l t & \cos\omega_l t & 0 \\ 0 & 0 & 1 \end{bmatrix} * \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix} * \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} = \begin{bmatrix} ? \\ ? \\ ? \end{bmatrix} \quad \textbf{(8)}$$

$$\begin{bmatrix} \cos\omega_l t & 0 & \sin\omega_l t \\ \sin\omega_l t & 0 & -\cos\omega_l t \\ 0 & 1 & 0 \end{bmatrix} * \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} = \begin{bmatrix} \sin\omega_l t \\ -\cos\omega_l t \\ 0 \end{bmatrix}$$

The result is the vector [sin(ωt)*$\mathbf{I}_x$, -cos(ωt)*$\mathbf{I}_y$, 0*$\mathbf{I}_z$].

Using operator formalism,

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

which is equal to

-$\mathbf{I}_y$.

Since cos π/2 = 0 and sin π/2 = 1. For the second rotation:

-$\mathbf{I}_y$ =$\omega_l t\hat{\mathbf{I}}_z$=> -$\mathbf{I}_y$ cos ω_lt + $\mathbf{I}_x$ sin ω_lt

Which is (whew!) the same as calculated by matricies.
Obviously, if the order of the rotations is reversed:

$\mathbf{I}_z$ =$\omega_l t\hat{\mathbf{I}}_z$=> =$\pi/2\hat{\mathbf{I}}_x$=>

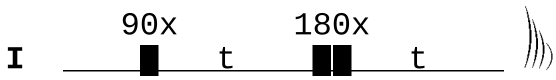
The answer is completely different.

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

The operator notation is essentially an expanded version of more compact matrix method. When the sequences become very complicated (reality) and there is no possibility for the luxury of simplification, then the matrix method is a very nice tool to use especially if a computer is available.

So as to not create too much confusion for those who know something about density matricies, the rotation matricies **are not** the *density matrix*. In fact, the *magnetization vector* is identical to the reduced spin density matrix. The rotation matricies presented here are related to unitary matricies called *superoperators*.

As an example how one might use the rotation matrices to simplify calculations consider a single isolated spin **I** subjected to the following pulse sequence:



Calculating this sequence by product operators:

$$\mathbf{I_z} \;\; =\pi/2\hat{\mathbf{I}}_\mathbf{x}\!=> \mathbf{-I_y} \;\; =\omega_I t\hat{\mathbf{I}}_\mathbf{z}\!=> \mathbf{-I_y} \cos \omega_I t + \mathbf{I_x} \sin \omega_I t$$

$$=\pi\hat{\mathbf{I}}_\mathbf{x}\!=> \mathbf{I_y} \cos \omega_I t + \mathbf{I_x} \sin \omega_I t$$

$$=\omega_I t\hat{\mathbf{I}}_\mathbf{z}\!=> (\ \mathbf{I_y} \cos \omega_I t - \mathbf{I_x} \sin \omega_I t\ ) \cos \omega_I t$$

$$+(\ \mathbf{I_x} \cos \omega_I t + \mathbf{I_y} \sin \omega_I t\ ) \sin \omega_I t$$

$$\equiv \mathbf{I_y}\,(\cos^2 \omega_I t + \sin^2 \omega_I t)$$

$$\equiv \mathbf{I_y}$$

With such a simple result, it would seem there should be a simpler way to calculate the sequence.

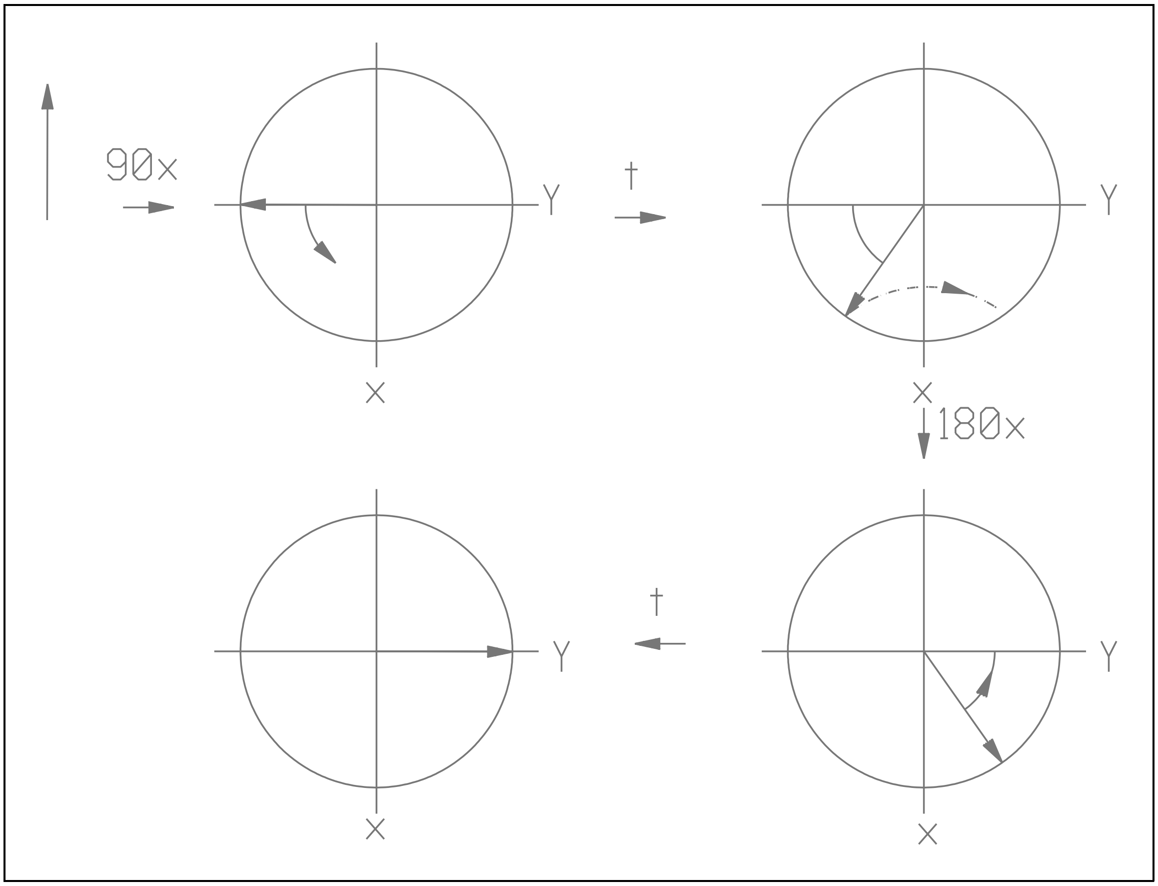


Figure 4.1. Vector representation of the refocusing effect of a 180° pulse placed in the center of free precession period.

If we look only at the rotations:

$=\pi/2\hat{\mathbf{I}}_x=> \ =\omega_I t\hat{\mathbf{I}}_z=> \ =\pi\hat{\mathbf{I}}_x=> \ =\omega_I t\hat{\mathbf{I}}_z=>$

We can simplify this sequence by modifying it in the following manner.
By introducing a rotation followed by the inverse of the same rotation we do no cause any net motion of the spin system. For example:

$=\pi\hat{\mathbf{I}}_x=> \ =-\pi\hat{\mathbf{I}}_x=>$

rotates the spin system by 180° then by -180°. The overall rotation is zero this is

$$\begin{array}{c}\begin{bmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix}\\ I_E\end{array}$$

equivalent to multiplication by the identity matrix $\mathbf{I_E}$. This can easily be demonstrated by multiplying two inverse matricies.

We can formally introduce these rotations anywhere in a pulse sequence. Using the above sequence:

$=\pi/2\hat{\mathbf{I}}_{\mathbf{x}}=> \underline{=\pi\hat{\mathbf{I}}_{\mathbf{x}}=> =\text{-}\pi\hat{\mathbf{I}}_{\mathbf{x}}=>} =\omega_{\mathbf{I}}t\hat{\mathbf{I}}_{\mathbf{z}}=> =\pi\hat{\mathbf{I}}_{\mathbf{x}}=> =\omega_{\mathbf{I}}t\hat{\mathbf{I}}_{\mathbf{z}}=>$

We have not accomplished anything. However, if we now look at the series of rotations underlined in the next sequence,

$=\pi/2\hat{\mathbf{I}}_{\mathbf{x}}=> =\pi\hat{\mathbf{I}}_{\mathbf{x}}=> \underline{=\text{-}\pi\hat{\mathbf{I}}_{\mathbf{x}}=> =\omega_{\mathbf{I}}t\hat{\mathbf{I}}_{\mathbf{z}}=> =\pi\hat{\mathbf{I}}_{\mathbf{x}}=>} =\omega_{\mathbf{I}}t\hat{\mathbf{I}}_{\mathbf{z}}=>$,

we can simplify the sequence by means of matrix algebra.

$$\begin{array}{ccc}\begin{bmatrix}1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & -1\end{bmatrix} & \begin{bmatrix}\cos\omega t & -\sin\omega t & 0\\ \sin\omega t & \cos\omega t & 0\\ 0 & 0 & 1\end{bmatrix} & \begin{bmatrix}1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & -1\end{bmatrix}\\ -\pi I_x & \omega t I_z & \pi I_x\end{array}$$

$$\begin{bmatrix}\cos\omega t & -\sin\omega t & 0\\ -\sin\omega t & -\cos\omega t & 0\\ 0 & 0 & -1\end{bmatrix}\begin{bmatrix}1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & -1\end{bmatrix}$$

$$\begin{array}{c}\begin{bmatrix}\cos\omega t & \sin\omega t & 0\\ -\sin\omega t & \cos\omega t & 0\\ 0 & 0 & 1\end{bmatrix}\\ -\omega t I_z\end{array}$$

The matrix multiplication shows that the sequence:

$=-\pi\hat{\mathbf{I}}_{\mathbf{x}}=>\ =\omega_{\mathrm{I}}t\hat{\mathbf{I}}_{\mathbf{z}}=>\ =\pi\hat{\mathbf{I}}_{\mathbf{x}}=>$

is equivalent to the single rotation:

$=-\omega_{\mathrm{I}}t\hat{\mathbf{I}}_{\mathbf{z}}=>$.

Substituting this rotation for the equivalent three rotations in the sequence:

$=\pi/2\hat{\mathbf{I}}_{\mathbf{x}}=>\ =\pi\hat{\mathbf{I}}_{\mathbf{x}}=>\ \underline{=-\omega_{\mathrm{I}}t\hat{\mathbf{I}}_{\mathbf{z}}=>}\ =\omega_{\mathrm{I}}t\hat{\mathbf{I}}_{\mathbf{z}}=>$

Now two inverse rotations are adjacent:

$=\pi/2\hat{\mathbf{I}}_{\mathbf{x}}=>\ =\pi\hat{\mathbf{I}}_{\mathbf{x}}=>\ \underline{=-\omega_{\mathrm{I}}t\hat{\mathbf{I}}_{\mathbf{z}}=>\ =\omega_{\mathrm{I}}t\hat{\mathbf{I}}_{\mathbf{z}}=>}$

And their product is equal to $\mathbf{I}_{\mathbf{E}}$. These rotations cancel, yielding:

$=\pi/2\hat{\mathbf{I}}_{\mathbf{x}}=>\ =\pi\hat{\mathbf{I}}_{\mathbf{x}}=>$

or simply

$=3\pi/2\hat{\mathbf{I}}_{\mathbf{x}}=>$

We have eliminated the $=\omega_{\mathrm{I}}t\hat{\mathbf{I}}_{\mathbf{z}}=>$ term completely and made the calculation much easier.

$\mathbf{I}_{\mathbf{z}}\ =3\pi/2\hat{\mathbf{I}}_{\mathbf{x}}=>\ \mathbf{I}_{\mathbf{y}}$

This sequence is referred to as a spin echo sequence, and is used to eliminate the chemical shift term, $=\omega_{\mathrm{I}}t\hat{\mathbf{I}}_{\mathbf{z}}=>$, during a period of a pulse sequence.