The Vector Paradigm in Modern NMR Spectroscopy:

I. Pulse Sequences Applied to Isolated Spin Systems.

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NMR spectroscopy was revolutionized in the mid 1970's with the introduction of two-dimensional methods by Richard Ernst for which, among other contributions, he won the 1991 Nobel prize in Chemistry. Since that time there has been an explosion of powerful methods that has made NMR an important player in many scientific fields. The majority of these methods were developed for the use in the determination of structures of biomolecules. Yet another Nobel prize in 2002 was awarded to Kurt Wuthrich for his contributions in this area. With the sequence of the human genome, among others, in hand, and the current structural genomics efforts around the world, large numbers of proteins and other biomacromolecules with unknown structures and function are now under investigation. NMR is playing a major role in answering the questions arising in the burgeoning field of proteomics.

The techniques of modern NMR spectroscopy are based on a large number of pulse sequences. Many of these experiments are extremely useful not only for the biomolecular NMR spectroscopist but also for the working chemist. NMR spectroscopy, as it is taught in undergraduate organic or analytical chemistry courses, is a good introduction, but the real power of NMR comes only with more sophisticated techniques. The descriptions of the advanced techniques are often couched in terms of density matrix theory or the equivalent product operator formalism. The product operator formalism, which was introduced in the early 1980s, is the most widely used technique for describing NMR pulse sequences. Once the concepts of the product operators are grasped, one can read a pulse sequence in a manner similar to that used to understand electronic schematics.
Prior to the introduction of the product operator formalism, for a complete description of the motion of nuclear spins subjected to magnetic fields one had to rely on the mathematics of the density matrix approach. While the density matrix is powerful and provides a complete description of the motion of nuclear spins, it is not readily visualized. Simple vector models of spin physics, which are easily visualized, are sufficient to accurately describe the motions of isolated spins, but fail to produce the correct results in scalar coupled spin systems. The product operator formalism simplifies the description of NMR experiments while retaining the mathematical rigor of density matrix theory.

The motion of isolated spins can be visualized by the simple vector model with no loss of rigor and can easily be mapped to the product operator approach. In and the following papers, the vector model in the framework of the product operator formalism will be used to describe the motion of isolated and coupled spin systems subjected to various pulse sequences. The description of the motion of isolated spin systems in this paper will serve as a jumping-off point for the extension of the vector model for visualization of the product operator treatment of coupled spin systems. With a working knowledge of the product operators for the description of isolated and coupled spin systems, one can tackle the complicated pulse sequences found in the literature with little more than pencil and paper. In fact, most pulse sequences can be understood, at least qualitatively, with mental gymnastics.

**The Vector Paradigm**

Vectors have been used from the early days of NMR to describe the motion of nuclear spins
subjected to a series of radiofrequency (RF) pulses and time delays. The behavior of the rotation of a three-dimensional vector completely describes (in high magnetic fields) the motion of nuclear spins subjected to both static and oscillating magnetic fields. Although the simple three-dimensional vector model *fails* to predict the behavior of spin systems in which there are interactions between spins, such as scalar coupling, the simplicity of the vector for describing the motion of nuclear spins is still extremely valuable. Even in the cases where the three-dimensional vector model breaks down, a clear understanding of vector rotations allows one to visualize the motion of vectors that represent coupled spin systems of higher dimensionality (e.g. 16 or greater dimensions in a spin system with two coupled spins). In order to understand complicated multipulse NMR experiments in coupled spin systems, intimate familiarity with the nature of the rotations of three-dimensional vectors is imperative.

At thermal equilibrium, individual nuclear magnetic moments precess about the Z axis of the external magnetic field at the Larmor frequency, \( \omega = \gamma B_0 \), where the magnetogyric ratio \( \gamma \) is a characteristic property of every nucleus and \( B_0 \) is the strength of the magnetic field. For nuclei with a nuclear spin of \( \frac{1}{2} \), which are the only spins to be considered in this paper, two energy states are available, \( \alpha \) and \( \beta \).
Boltzmann equilibrium of the states is established when the nucleus is put into an external magnetic field. Since there is a slight population excess of spins in the lower energy level, there is a net group of spins that give rise to a bulk magnetic moment. The vectors that represent individual nuclear magnetic moments precess in a cone around the Z axis (Figure 1). The bulk magnetization of the sample is the vector sum of all of the individual precessing nuclear magnets. The summed vector has a non-vanishing component only along the Z axis. The projection of the vectors in the XY plane is zero, since all possible orientations (phases) of the vectors around the Z axis are allowed and destructive interference among the individual spin vectors occurs. The vectors are said to precess incoherently since the phase relationships between the individual spin vectors is arbitrary. As long as the nuclear spin system consists of identical and non-interacting nuclei, the exact behavior (motion) of the spin system can be described by transformations of the three-dimensional vector that represents the bulk magnetization, even in the presence of relaxation processes. (Appendix I-Bloch to rotation matrix). If relaxation is ignored, the transformations become simple 3D rotation matrices. In the following treatment relaxation will not be considered.

**NMR and Rotations**

Every interaction in NMR spectroscopy, e.g. chemical shift, scalar coupling, and RF pulses, can be formally represented as a rotation or sequence of rotations of a vector. All orthogonal rotations of any vector involve a maximum of three coordinates: the axis about which the vector is rotated and the two axes that are orthogonal (90°) to the rotation axis. However, in NMR the dimension of the state vector which describes the spin system can be quite large. As will be
presented in the next paper of this series, a 16 dimensional vector is needed to describe the 

motion of two coupled spins and a 64 dimensional vector is required for a three coupled spins.

However, all rotations of these vectors occur in three dimensional subspaces that involve only 
one rotation axis and two orthogonal axes. Many of these subspaces have no physical analog, 

but since they are three-dimensional rotations, a picture of the rotations can be constructed by 

using a three-dimensional framework with the appropriate labels for the axes. This all may seem 

very esoteric at this point, but as we proceed, rotations of multidimensional vectors will become 

quite familiar and useful for the description of NMR pulse sequences.

Isolated spin systems interact only with radiofrequency (RF) pulses and the chemical shift 

operator. There are no scalar couplings or other interactions other than relaxation processes with 

any other spins. Isolated spin systems act as a single entity even though the system consists of a 

very large number (~10^{17}) of individual spins. There are not many good examples of truly 

isolated spin systems among common compounds. ^3He and ^{129}Xe are representatives of truly 

isolated spin \( \frac{1}{2} \) systems. Two examples considered to be isolated spins systems are the protons in 

^{12}C^{1}HCl_3 and ^1H_2^{16}O. The proton in ^{13}C depleted chloroform is not really isolated since the 

chlorine atoms have a nuclear spin of 3/2 and are scalar coupled to the protons, but those 

interactions are very small because the rapid quadrupolar relaxation of the chlorine nuclei 

effectively decouples the chlorine spins from those of the proton. We will not consider systems 

with spin greater than 1/2. In water depleted of ^{17}O, which has a spin of 5/2, the two protons are 

magnetically equivalent (they have identical chemical shifts) and so they can be treated as a 

single isolated system. The state of an isolated magnetization vector, \( \mathbf{I} \), can be described by the
components of a vector in a three-dimensional Cartesian coordinate system (Figure 2). For spin \( \mathbf{I} \), these components are \( a^*\mathbf{I}_x \), \( b^*\mathbf{I}_y \), and \( c^*\mathbf{I}_z \), where \( \mathbf{I}_x \), \( \mathbf{I}_y \), and \( \mathbf{I}_z \) are unit vectors. Any vector can be represented as a vector sum of unit vectors, which lie along the coordinate axes. The vector sum \( a^*\mathbf{I}_x + b^*\mathbf{I}_y + c^*\mathbf{I}_z \) represents a vector in three-dimensional space that has components (projections of the vector onto the reference coordinate axes) of magnitude \( a \) along the X axis, \( b \) along the Y axis, and \( c \) along the Z axis. The bulk magnetization vector that lies along the Z axis of the external magnetic field can be described by the vector \((0^*\mathbf{I}_x, 0^*\mathbf{I}_y, 1^*\mathbf{I}_z)\). In the absence of relaxation, the magnitude of the magnetization remains constant. We will assume that the magnetization is normalized and therefore length of the vector is unity.

In order to be mathematically complete, there is a component, represented by the identity element \( \mathbf{I}_E \), which corresponds to the remainder of the spin system that is not involved in the bulk magnetization. This

**Figure 2.** A unit vector \( \mathbf{I} \) decomposed into three orthogonal components \((a^*\mathbf{I}_x, b^*\mathbf{I}_y, c^*\mathbf{I}_z)\). The angles \( \phi \) and \( \theta \) are polar coordinates.

**Table 1.** Direction of rotations in a right-handed coordinate system.

<table>
<thead>
<tr>
<th>Positive rotation about Y:</th>
<th>Z → X → -Z → -X → Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive rotation about X:</td>
<td>Z → -Y → -Z → Y → Z</td>
</tr>
<tr>
<td>Positive rotation about Z:</td>
<td>X → Y → -X → -Y → X</td>
</tr>
</tbody>
</table>
component corresponds to the majority of spins that have equal numbers in the upper and lower quantum mechanical energy levels. The spin vectors from these spins cancel exactly and do not contribute to the NMR magnetization. The symmetry of this component is spherical and, therefore, is invariant to any rotation. The rotational invariance suggests that in most cases we can totally ignore this component. However, it will become important when we generate the model for coupled spin systems. The complete vector description of an isolated spin system is 4 dimensional, \((\mathbf{I}_E, \mathbf{I}_x, \mathbf{I}_y, \mathbf{I}_z)\), but since \(\mathbf{I}_E\) does not supply useful information we will use only the three Cartesian coordinates,\((\mathbf{I}_x, \mathbf{I}_y, \mathbf{I}_z)\). In the state vector for any spin system, isolated or not, there will always be an identity component that is invariant to rotation.

**Right-handed Cartesian coordinates**

The X, Y, and Z coordinates 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 \(X \otimes Y\) results in a vector aligned along the positive Z axis. In this coordinate system, a positive rotation of a Z vector about the Y axis will carry the vector towards the positive X axis (Table 1). 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*. (##) All positive rotations in this convention are counterclockwise around the rotation axis.
In all rotations of the state vector, only components that are orthogonal (at right angles) to the axis of rotation are affected. In a simplified treatment of NMR spectroscopy that neglects the effects of being off-resonance, 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 due to the oscillating magnetic field of RF pulses. As a spectroscopist, these are the only available interactions with the spin system.

If a Z vector representing the equilibrium magnetization of spin $I$, $(0*I_x, 0*I_y, 1*I_z)$ or simply $I_z$, is rotated about the X axis by $90^\circ$ ($\pi/2$ radians), the vector will lie along the -Y axis and be represented as -$I_y$ (Figure 3). If the rotation angle is increased to $180^\circ$ ($\pi$ radians), then the initial vector $I_z$ will rotate to the -Z axis (-$I_z$). Obviously, a $360^\circ$ (2$\pi$ radians) rotation will return

$$ I_z \overset{\pi/2}{\rightarrow} -I_y $$

Figure 3. Rotations of vector $I$ by $\pi/2$, $\pi$, and $2\pi$ about the X axis.
the vector to the starting position along the Z axis ($I_z$).

A positive rotation by $90^\circ (\pi/2)$ about the X axis of a vector initially along the Z axis will be designated by the notation shown in Eqn (1) where the initial state of the spin system is represented by $I_z$, the rotation $\pi/2T_x$ is placed over an arrow, and the final state is represented by $-I_y$.

The rotation operator $\pi/2T_x$, gives information about the angle of rotation ($\pi/2$) and the rotation axis (X). Letters with a circumflex represent rotation operators. A smaller rotation of say $60^\circ$ 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 resort to simple trigonometry. Figure 4 shows the trigonometric relationships of the components of a vector that is tilted away from the Z axis toward the Y axis by $60^\circ (\pi/3)$. The coefficient of the Z component $I_z$ is equal to $\cos(60^\circ)$ and that of the Y component $-I_y$ is equal to $\sin(60^\circ)$. The notation for a $60^\circ (\pi/3)$ rotation of the $I_z$ spin vector about the X axis is given in Eqn. (2).

$$I_z \xrightarrow{\frac{\pi}{3} \hat{i}_x} I_z \cos\left(\frac{\pi}{3}\right) - I_y \sin\left(\frac{\pi}{3}\right)$$

Figure 4. Components of a vector, initially aligned along the Z axis, rotated by $\pi/3 (60^\circ)$ around the X-axis. The -Y component is $\sin(\pi/3)$ and the Z component is $\cos(\pi/3)$. 
Note that the rotation is positive, that is, the Z component of \( \mathbf{I} \) rotates toward the \(-Y\) axis with a positive rotation about the X axis. Equation (3) is the notation for the general rotation, \( \theta \) about the X axis.

\[
\mathbf{I}_z \xrightarrow{\theta \hat{x}} \mathbf{I}_z \cos(\theta) - \mathbf{I}_y \sin(\theta)
\]

(3)

If \( \theta \) is \( 3\pi/2 \) (270°), \( \sin(3\pi/2) = -1 \) and the final position for the vector is along the positive Y axis (Eqn. 4).

\[
\mathbf{I}_z \xrightarrow{3\pi/2 \hat{x}} \mathbf{I}_z \cos\left(\frac{3\pi}{2}\right) - \mathbf{I}_y \sin\left(\frac{3\pi}{2}\right) = \mathbf{I}_z \ast 0 - \mathbf{I}_y \ast 1 \equiv \mathbf{I}_y
\]

(4)

The same result would be obtained by rotating the \( \mathbf{I}_z \) vector by \(-\pi/2\) about the same axis, as show in Eqn. 5.

\[
\mathbf{I}_z \xrightarrow{-\pi/2 \hat{x}} \mathbf{I}_y
\]

(5)

The most commonly used pulsed NMR experiment consists of a single \( \pi/2 \) radio frequency (RF) pulse, which rotates the magnetization from the Z into the XY plane, followed by the detection of the spins during the acquisition period, during which the spin vectors precess at their characteristic frequencies (chemical shifts) about the Z axis. During the acquisition time, the receiver in the NMR spectrometer is turned on; the signal is detected and digitized. The digitized signal is then Fourier transformed to give the familiar one-dimensional NMR spectrum with each
of the individual spins giving rise to a line in the NMR spectrum.

Figure 5 is a vector picture of the single pulse experiment. The initial rotation of 90° around the X axis places the vector along the -Y axis. During the acquisition time, t, the individual spin vectors precess around the Z axis at a rate \( \omega_l \). The total angle that the vectors traversed in a given time is given by the product of the frequency and the time, \( \omega_l t \). The operator sequence depicting this experiment is given in Eqn. 6.

\[
\begin{align*}
I_z & \xrightarrow{-\frac{\pi}{2}I_x} -I_y \\
& \xrightarrow{\omega_l I_z} -I_y \cos(\omega_l t) + I_x \sin(\omega_l t)
\end{align*}
\]

The Fourier transform of the signal detected in quadrature (two simultaneous, orthogonal channels) would give an NMR resonance line at the frequency \( \omega \).

**Rotation Matrices**

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

Equation 7 is the matrix representation for the rotation of a magnetization vector $\mathbf{I}$, consisting of three Cartesian components $I_x$, $I_y$, and $I_z$, by an angle $\theta$ about the X axis. The matrix with 3 rows and 3 columns (3 X 3) is the rotation matrix and it operates on the 1 X 3 row vector that represents the magnetization vector.

To review, multiplication of a row vector and a matrix is performed as follows: The vector is multiplied, element by element, with the first column of the matrix and the sum of the products becomes the first element in the resultant vector. The row vector times the second matrix column gives the middle element of the resultant vector and likewise for the third element. Equation 8 shows the general case.
If a vector, \( \mathbf{I} \), has the components \([0*I_x, 0*I_y, 1*I_z]\) or \(I_z\), then a rotation of \(\pi/2\) \(\mathbf{I}_x\) would be represented as in Eqn. 9.

Substituting \(\cos(\theta/2) = 0\) and \(\sin(\theta/2) = 1\), the result is \([0*I_x, -1*I_y, 0*I_z]\) or \(-\mathbf{I}_y\).

As shown above in Eqn. (1), in operator notation the sequence is represented as in Eqn. (10).

\[
\begin{bmatrix}
1 & 0 & 0 \\
0 & \cos(\pi/2) & \sin(\pi/2) \\
0 & -\sin(\pi/2) & \cos(\pi/2)
\end{bmatrix}
\begin{bmatrix}
1 & 0 & 0 \\
0 & 0 & 1 \\
0 & -1 & 0
\end{bmatrix}
= \begin{bmatrix}
1 & 0 & 0 \\
0 & 0 & 1 \\
0 & -1 & 0
\end{bmatrix}
\]

Substituting \(\cos(\pi/2) = 0\) and \(\sin(\pi/2) = 1\), the result is \([0*I_x, -1*I_y, 0*I_z]\) or \(-\mathbf{I}_y\).

As shown above in Eqn. (1), in operator notation the sequence is represented as in Eqn. (10).

\[
\mathbf{I}_z \xrightarrow{\pi/2 \mathbf{I}_x} \mathbf{I}_z \cos(\pi/2) - \mathbf{I}_y \sin(\pi/2) \equiv -\mathbf{I}_y
\]

The rotation matrices for vector rotations around the X, Y, and Z coordinate axes are given in Eqn. 11.
In most pulse sequences, there is more than one rotation. As an example, consider the single pulse sequence described above (Eqn. 6) that rotates $I_z$ by $90^\circ$ about the X axis followed by a rotation of an angle $\omega t$ about the Z axis caused by a chemical shift. These rotations in matrix notation are shown in Eqn. 12.

\[
\begin{bmatrix}
1 & 0 & 0 \\
0 & \cos(\theta) & \sin(\theta) \\
0 & -\sin(\theta) & \cos(\theta)
\end{bmatrix}
\begin{bmatrix}
\cos(\theta) & 0 & -\sin(\theta) \\
0 & 1 & 0 \\
\sin(\theta) & 0 & \cos(\theta)
\end{bmatrix}
\begin{bmatrix}
\cos(\phi) & \sin(\phi) & 0 \\
-\sin(\phi) & \cos(\phi) & 0 \\
0 & 0 & 1
\end{bmatrix}
\]

(11)

\[
\theta \hat{I}_x \rightarrow \theta \hat{I}_y \rightarrow \phi \hat{I}_z
\]

Note that the order of time sequential matrices is from left to right. The first rotation is the matrix to the immediate right of the row vector and the next rotation matrix is placed to the right of the first. The order of rotations is very important (commutative property). An entirely different result would be obtained if the rotation order was $\omega t \hat{I}_z$ then $\pi / 2 \hat{I}_x$. In this case, the first rotation would not change the orientation of $I_z$ and the $\pi/2$ rotation about the X axis would
leave the vector along the \(-Y\) axis. However, once the physical order of matrices (rotations) is established, the order of multiplication is irrelevant (distributive property). The leftmost matrix can multiply the row 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. As a refresher, Eqn. 13 shows the general method for multiplying matrices.

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

For the single pulse experiment (Fig. 5), we can calculate the rotation of the sequence by the use of matrices (Eqns. 14).

The result is the vector \([\sin(\omega t)\mathbf{i}_x, -\cos(\omega t)\mathbf{i}_y, 0\mathbf{i}_z]\), which is identical to the result calculated above using the operator formalism (Eqn. 6). The operator notation is essentially a shorthand method for matrix multiplication.

\[
\begin{bmatrix}
1 & 0 & 0 \\
0 & \cos(\frac{\pi}{2}) & \sin(\frac{\pi}{2}) \\
0 & -\sin(\frac{\pi}{2}) & \cos(\frac{\pi}{2})
\end{bmatrix}
\begin{bmatrix}
\cos(\omega t) & \sin(\omega t) & 0 \\
-\sin(\omega t) & \cos(\omega t) & 0 \\
0 & 0 & 1
\end{bmatrix}
= 
\begin{bmatrix}
? & ? & ?
\end{bmatrix}
\]

\[
\begin{bmatrix}
1 & 0 & 0 \\
0 & 0 & 1 \\
0 & -1 & 0
\end{bmatrix}
\begin{bmatrix}
\cos(\omega t) & \sin(\omega t) & 0 \\
-\sin(\omega t) & \cos(\omega t) & 0 \\
0 & 0 & 1
\end{bmatrix}
= 
\begin{bmatrix}
? & ? & ?
\end{bmatrix}
\]
Algorithmic approach

In practice, an algorithmic approach to the rotation of the magnetization vector simplifies the process. 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 starting vector by \( \cos(\angle) \) and adding \( \sin(\angle) \) times the vector obtained by the cross product of the rotation axis into the initial vector. The direction of the resultant vector of the cross product can obtained from the right hand rule by 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.

An example is probably the easiest way to demonstrate these rules. Take the following sequence of rotations in Eqn. 15.

\[
\begin{bmatrix}
\cos(\omega t) & \sin(\omega t) & 0 \\
0 & 0 & 1 \\
\sin(\omega t) & -\cos(\omega t) & 0
\end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} = \begin{bmatrix} \sin(\omega t) \\ -\cos(\omega t) \\ 0 \end{bmatrix}
\]

\( I_Z \xrightarrow{\theta \hat{I}_X} ? \xrightarrow{\omega t \hat{I}_Z} ? \xrightarrow{\gamma \hat{I}_y} ? \) (15)

The initial magnetization is at thermal equilibrium along the Z axis \( (I_Z) \). The magnetization is
first tipped by an angle of $\theta$ around the X-axis, it then precesses by an angle $\omega t$ around the Z axis, and is finally rotated by an angle of $\gamma$ around the Y axis.

Figure 6 represents the motion of a 3 dimensional vector initially aligned along the Z axis subjected to this series of rotations. Starting with the vector $\mathbf{I}_z$, rotate, using the right-hand rule, around the X axis by an angle $\theta$. $\mathbf{I}_z$, the initial vector, is multiplied by $\cos(\theta)$ and the final vector, $-\mathbf{I}_y$, is multiplied by $\sin(\theta)$ (Eqn 16).

\[
\mathbf{I}_z \xrightarrow{\theta \hat{x}} \mathbf{I}_z \cos(\theta) - \mathbf{I}_y \sin(\theta)
\]

(16)

The next rotation of $\omega t \hat{z}$ is shown in Eqn.17.
Each of the components, \( I_z \) and \( I_y \), are treated independently. The \( I_z \) component is not affected by a rotation about the parallel Z axis. The rotation carries the -\( I_y \) component towards the \( I_x \) axis with the appropriate cosine and sine multipliers. Notice that the components retain the multipliers that were attached during the first rotation. The final rotation is calculated in Eqn. 18, which is further simplified by collecting terms.

\[
I_z \cos(\theta) - I_y \sin(\theta) \rightarrow \frac{\hbar \omega t Z}{Z} \\
I_z \cos(\theta) + [-I_y \cos(\omega t) + I_x \sin(\omega t)] \sin(\theta) 
\]

In these calculations, it is apparent that one quickly can become mired in a huge number of trigonometric functions and spin operators, which tends to degrade the simplicity of this formalism. The use of a computer can eliminate the difficulty at the expense of a loss of understanding. However, the best approach is to introduce simplifications, which do not compromise accuracy, but retain overall clarity for a sequence of rotations. However, at times it
is necessary to bite the bullet and just do the entire calculation.

Composite rotations

In this section of the paper, we return to the matrix multiplication method to show how some complicated pulse sequences can be greatly simplified by a few manipulations of the rotation matrices. These composite rotation methods are extremely important in the analysis of complicated pulse sequences.

One of the most widely used multiple pulse sequences is the spin echo. This pulse-interrupted free precession sequence consists of a time delay during which free precession about the Z axis due to chemical shift or magnetic field inhomogeneities occurs, a $\pi$ rotation, and finally another time delay with free precession about the Z axis for a time identical in length to the first delay. The initial state of the magnetization typically lies in the XY plane. The effect of the spin echo is to eliminate all rotations around the Z axis at the echo that occurs at the end of the second free precession delay. This is equivalent to eliminating, on average, the rotations due to chemical shift and/or magnetic field inhomogeneities during the sequence. This does not imply that chemical shift does not occur during the delays, but that at the special, end point of the spin echo sequence, the position of the spin vectors, which can have different precession frequencies, does not depend on the individual chemical shifts. That is all of the spin vectors are aligned.
Consider a race in which there are some fast, medium and slow runners. At the beginning of the race all of the competitors are lined up at the starting line. The gun sounds and the race is on. The faster runners speed ahead of the slower runners with the very slowest of them at the rear of the pack. This, however, is a rather unusual race in that at a given time the gun is fired again. At that time the runners stop, turn around, and run back toward the starting line. For the fastest runners, the distance back to the starting line is further than that of the medium runners and obviously the very slowest runner has the shortest distance to run. Now assuming that each runner maintains the exact same speed in the return leg of the race, all of the runners will reach the starting line at the same time. This is the echo. In NMR spectroscopy, the nuclei in a molecule all have different frequencies (chemical shifts). Once the spins are excited with a pulse (Fig. 7A) they begin to precess around the Z axis (Fig. 7B). Each spin vector starts at the same location but because of the different frequencies will transverse a different angle around the Z axis in a given time period $t_1$ (Fig. 7C). A $\pi$ pulse (along the Y axis in this
example) between positions C and D in Fig. 7 reverses the direction of the precession for each of
the spins (Fig. 7e). After the time $t_2$ all of the vectors realign (Fig. 7F). The calculation of this
sequence using product operators starting after the initial $\pi/2$ pulse is given in Eqn. 19.

$$
-I_y \overrightarrow{ztI} \rightarrow -I_y \cos(\omega t_1) + I_x \sin(\omega t_1)
$$

$$
\pi \overrightarrow{ytI} \rightarrow -I_y \cos(\omega t_1) - I_x \sin(\omega t_1)
$$

$$
\omega t_1 \overrightarrow{ytI} \rightarrow \left[ -I_y \cos(\omega t_2) + I_x \sin(\omega t_2) \right] \cos(\omega t_1)
$$

$$
+ \left[ -I_x \cos(\omega t_2) - I_y \sin(\omega t_2) \right] \sin(\omega t_1)
$$

$$
\equiv -I_y \left[ \cos(\omega t_1) \cos(\omega t_2) + \sin(\omega t_1) \sin(\omega t_2) \right]
$$

if $t_1 = t_2$

$$
\equiv -I_y \left[ \cos^2(\omega t) + \sin^2(\omega t) \right] = -I_y
$$

This simple result is totally independent of the frequencies of the spin vectors. Just as in the race,
all of the runners arrive at the start/finish line at the same time. It would seem that with such a
simple result, it would seem that there should be an easier way to calculate this pulse sequence.

One obvious result of the calculation is that formally the spin echo is equivalent to a $0^\circ$ rotation
about the Y axis. This simplicity continues if the phase of the $\pi$ pulse is switched from the Y axis
to the X axis. Both vector pictures and operator calculations show that this pulse sequence is
equivalent to a $\pi$ rotation about the X axis. The demonstration of this is left to the reader.

Matrix algebra can lead us to an easy method for simplifying operator calculations. Using the
spin echo sequence as an example, manipulations of the rotation operators can lead to drastic
simplification. Assuming $t_1 = t_2 = t$, Equation 20 is the time ordered list of the rotation operators for the spin echo sequence.

\[
\omega t \hat{I}_z \rightarrow \pi \hat{I}_y \rightarrow \omega t \hat{I}_z
\]  \hspace{1cm} (20)

Any rotation followed by the inverse of the same rotation causes no net motion of the spin system. For example, Eqn. 21 is a $\pi$ rotation around the Y axis followed by a $-\pi$ rotation about the same axis. A $\pi$ rotation is equal to a $-\pi$ rotation, but here the negative sign is explicitly included to show the general form.

\[
\pi \hat{I}_y \rightarrow -\pi \hat{I}_y
\]  \hspace{1cm} (21)

Intuitively, this rotation will return the magnetization vector to its initial position, since the sequence rotates the spin system one way and then just reverses that rotation. The overall rotation is zero; this is equivalent to multiplication by the identity matrix $I_E$. This can easily be demonstrated by multiplying the two matrices as shown in Eqn. 22.

\[
\begin{bmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{bmatrix}
\begin{bmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{bmatrix}
= 
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\]  \hspace{1cm} (22)

Multiplying any matrix by the identity matrix returns the original matrix unchanged. We can formally introduce an identity rotation anywhere in a pulse sequence. This little trick is useful in simplifying the calculation of a series of rotations. As an example, in the spin echo sequence we
insert a $\pi \hat{T}_y : -\pi \hat{T}_y$ sequence before the first precession about Z (Eqn.23).

\[
\begin{array}{cccccc}
\pi \hat{T}_y & -\pi \hat{T}_y & \omega t \hat{I}_z & \pi \hat{T}_y & \omega t \hat{I}_z \\
\end{array}
\]  
(23)

We have not done anything to the overall sequence by introducing these rotations. Experimentally this is almost true; there will be a slight perturbation due to the finite width of the pulses. The series of rotations enclosed in brackets shown in Eqn. 24, can be simplified by means of matrix algebra.

\[
\begin{array}{cccccc}
\pi \hat{T}_y & -\pi \hat{T}_y & \omega t \hat{I}_z & \pi \hat{T}_y & \omega t \hat{I}_z \\
\end{array}
\]  
(24)

Through multiplication of the appropriate matrices for this sequence (Eqns. 36-37), we find that the sequence of three operators can be replaced by a single negative rotation of an angle $\omega t$ around the Z axis (Eqn. 25).

\[
\begin{bmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1 \\
\end{bmatrix}
\begin{bmatrix}
\cos(\omega t) & \sin(\omega t) & 0 \\
-\sin(\omega t) & \cos(\omega t) & 0 \\
0 & 0 & 1 \\
\end{bmatrix}
\begin{bmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1 \\
\end{bmatrix}
\]  
(25)

The result from Eqn. 25 indicates that the bracketed sequence of Eqn. 24 can be simplified as in
Eqn. 26.

\[
\pi \hat{I}_y \rightarrow -\omega t \hat{I}_z \rightarrow \omega t \hat{I}_z
\]  \hspace{1cm} (26)

The two adjacent \( \hat{I}_z \) rotations (bracketed in Eqn. 27) are inverses, and their product is \( \mathbf{I}_E \).

\[
\pi \hat{I}_y \rightarrow \left[ -\omega t \hat{I}_z \rightarrow \omega t \hat{I}_z \right]
\]  \hspace{1cm} (27)

Since \( \mathbf{I}_E \), does not affect the spin system it can be eliminated leaving the single \( \pi_y \) rotation in Eqn. 28.

\[
\pi \hat{I}_y
\]  \hspace{1cm} (28)

This is the result anticipated from the vector picture and the full calculation above.

This composite rotation approach is general; whenever there a spin echo sequence either alone or embedded in a larger pulse sequence, during the period of the spin echo sequence, on average, there will be no net chemical shift (nor effects from inhomogeneous magnetic field) experienced by the spins involved. There may be a phase shift depending on the phase of the \( \pi \) pulse. Another point to consider is that the manipulation of the rotation operators was carried out independently from the spin vectors. This implies that this simplification is valid for any initial spin state.

\[
I_z \rightarrow \pi \hat{I}_y \rightarrow -I_z
\]  \hspace{1cm} (29)

If for example, there was no \( \pi/2 \) pulse at the beginning of the sequence in Fig. 7, then the initial state for the spin echo sequence would be \( \mathbf{I}_z \). From Eqn. 28, this would lead to the result in Eqn. 29. Again this fits with both the vector picture and the full calculation (not shown).
Spin echoes and pulsed field gradients

Imperfections in pulses can lead to unexpected peaks (artifacts) in NMR spectra. One technique to suppress these imperfections that is in common use is the pulsed field gradient. Physically, an inhomogeneous (usually linear) magnetic field is turned on for a short period of time. The field gradient causes spins in different parts of the sample experience different magnetic field strengths and thus different resonance frequencies. Figure 8 is a cartoon of the effect of a field gradient to a sample of identical spins. The vertical axis refers to the vertical spatial dimension of the sample in an NMR tube. In Figure 8A, shows the response of a magnetization vector with a rotating frame frequency of 0 Hz. No precession is observed over the time $t$. Figure 8B depicts the behavior of the spins in different parts of the spatially varying magnetic field strength during a pulsed field gradient. Magnetization in different parts of the sample experience different magnetic fields and precess according to frequency given by $\gamma I B_G(r)$, where $\gamma_I$ is the magnetogyric ratio of I and $B_G(r)$ is the spatially varying magnetic field. Once the field gradient...
is removed, the precession frequency will return to 0 Hz and no further precession will occur.

The vectors, however, will retain the phase that they acquired while the field gradient was being applied. A vertical projection of the vectors after the field gradient is removed is depicted in figure 8C. The vector sum is zero and no signal will be detected.

The rotation for a spatially varying magnetic field is shown in Eqn. 30. This rotation is very similar to that of the chemical shift operator $\omega_I t I_z$ as in Eqn. 6.

$$-I_y \gamma_G B_G(r) t I_z \rightarrow -I_y \cos(\gamma B_G(r) t) + I_x \sin(\gamma B_G(r) t)$$

(30)

In the same way that a spin echo sequence (Fig. 7 and Eqn. 19) refocuses the chemical shift of an isolated spin, that pulse sequence can be used to refocus the magnetization vectors dephase by a pulsed field gradient (PFG). Figure 9 is the pulse sequence and vector picture for this experiment. The PFGs can be placed anywhere within the free precession period, however in order to attain refocusing the area under the two PFGs must be identical. Using the same methods that were used to simplify the spin echo refocusing of chemical shift, a simple composite rotation can be obtained for the dephasing due to the PFGs (Eqns. 31). As would be expected, this sequence simultaneously refocuses any evolution due to chemical shift (Eqns. 31).

$$\frac{\pi}{2} I_x \rightarrow \omega_I t I_z \rightarrow \gamma_G B_G(r) t I_z \rightarrow \pi I_x \rightarrow \gamma_G B_G(r) t I_z \rightarrow \omega_I t I_z$$

= $$\frac{\pi}{2} I_x \rightarrow \pi I_x \rightarrow -\omega_I t I_z \rightarrow \gamma_G B_G(r) t I_z \rightarrow -\omega_I t I_z$$

= $$\frac{3\pi}{2} I_x$$

(31)
One might note that if the spin physically moves vertically in the sample tube during the spin echo period, the frequency that is applied by the PFG at the end of the spin echo will not in general be the same as that applied at the beginning. There will be loss of signal in this case and this is the basis for measuring diffusion coefficients of molecules in solution by NMR spectroscopy.

Conclusion

In this paper, the vector model for describing the motion of nuclear spin in isolated spin systems subjected to a sequence of radio frequency pulses and time delays is presented. The rotations of the magnetization vector are related to the product operator formalism and to three dimensional rotation matrices. With the aid of the rotation matrices, many multiple pulse sequences can be simplified by the use of composite rotations, where multiple steps in a pulse sequence are replaced with one or a few simpler steps in order to ease the analysis of the pulse sequence. This approach can be used in general for the analysis of other NMR spectroscopic techniques such as off-resonance effects, water suppression sequences, and relaxation processes. In the next paper of this series, the vector paradigm will be extended to spin systems with scalar (nuclear spin-spin) coupling.