2. The Vector Paradigm

In order to understand the behavior of nuclear spins subjected to radiofrequency pulses, the vector is an extremely useful tool. Although the simple vector model *fails* to predict the behavior of spin systems in which there are interactions such as scalar coupling, the simplicity of the vector for describing the motion is unsurpassed. The descriptions of NMR experiments that we will analyze will rely heavily on the use of the vector model whenever possible. Even in the cases where the vector model breaks down, having a clear understanding of vector rotations allows one to visualize the motion of vectors that represent spin systems of high dimension (e.g. 16 or greater dimensions). In order to understand complicated multipulse NMR experiments in coupled spin systems, intimate familiarity with the nature of the rotations of 3 dimensional vectors is imperative.

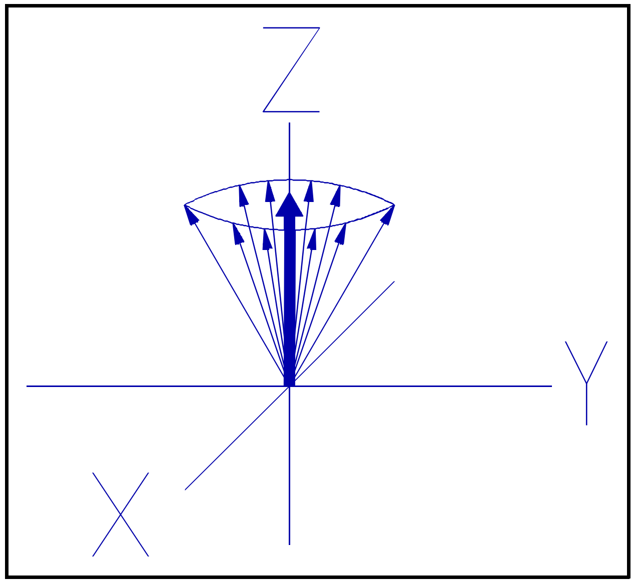

Figure 2.1. Individual nuclear magnetic moments precess in an external field giving rise to a net magnetic moment along the Z axis.

At thermal equilibrium, individual nuclear magnets precess with a Larmor frequency, ω, about the Z axis of the external magnetic field. Since there is a slight population excess of spins in the lower energy level, there will be a net group of spins that give rise to a bulk magnetic moment. The precessing vectors that represent individual nuclear magnetic moments form a cone around the Z axis (Figure 2.1). 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 spins 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 noninteracting nuclei, the *exact* behavior (motion) of the spin system can be described by rotations of the three dimensional vector that represents the bulk magnetization. This is where we begin the journey into spin gymnastics.

2.1 NMR and Rotations

Every interaction in NMR spectroscopy of liquids, 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. In NMR the dimension of the *state vector* which describes the spin system can be quite large. As we will see, a 16 dimensional vector is needed to describe the motion of a coupled two spin system and a 64 dimensional vector is required for a coupled three spin system. 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 commonplace and descriptive.

Isolated spin systems interact only with RF pulses and the chemical shift operator. There are no scalar couplings or other interactions with any other spins. Isolated spin systems act as a single entity even though the system consists of a very large number ($\sim 10^{17}$) of individual spins. Examples of isolated spins systems would be the protons in $^{12}C^{1}HCl_3$ and $^{1}H_2{}^{16}O$. The proton in ^{13}C depleted chloroform is not really isolated since the chlorines have nuclear spins, but the interactions are very small. In ^{17}O depleted water, the two protons are magnetically equivalent (they have exactly the same chemical shift) and so they can be treated as an isolated system. The behavior of the magnetization of an isolated spin system can be *exactly* described by the rotations of a vector in ordinary three dimensional space. The state of an isolated magnetization vector, **I**, can be described by the components of the vector in a three dimensional Cartesian coordinate system (Figure 2.2). For spin **I**, these components are $\mathbf{I_x}$, $\mathbf{I_y}$, and $\mathbf{I_z}$. Any vector can be represented as a vector sum of unit vectors that lie along the coordinate axes. The 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.

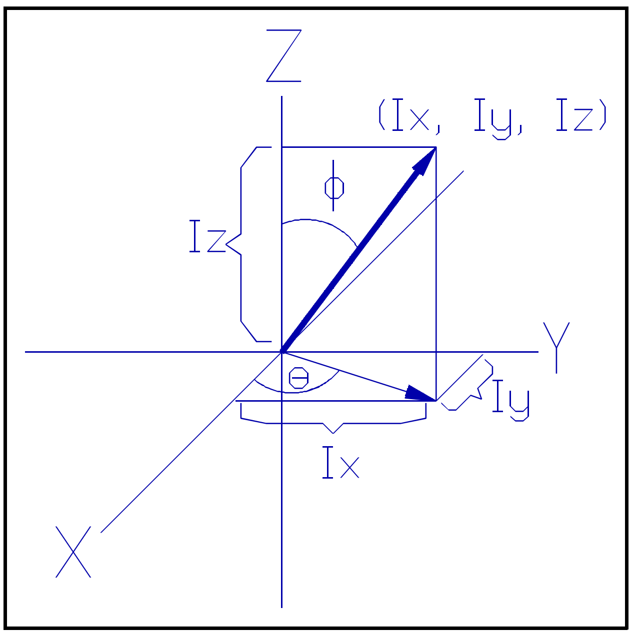

Figure 2.2. A unit vector **I** decomposed into three orthogonal components ($\mathbf{I_x}$, $\mathbf{I_y}$, $\mathbf{I_z}$). The angles ϕ and θ are polar coordinates.

In order to be mathematically complete, there is a component, the identity element $\mathbf{I_E}$, which describes the bulk of the spin system that is not involved in magnetization. This component corresponds to the majority of the spins that have equal numbers in the upper and lower quantum mechanical energy levels. The shape or *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. 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.