

### 13. Theoretical Description of Coupling - Product Operators

For an ensemble of noninteracting spins in a magnetic field, the classical description of the magnetization as a vector gives results identical to the quantum mechanical description given by the density matrix treatment. It is only in the presence of scalar coupling or other strictly quantum mechanical interactions (dipolar, quadrupolar, etc.) that the evolution of a spin system can not be described by classical mechanics. However, since most of the interesting and useful cases in modern NMR spectroscopy involve quantum mechanical interactions, the vector model must be abandoned or modified.

An intermediate approach to the description of NMR experiments involving scalar coupling is to use a classical vector model supplemented with results from quantum mechanics (See Benn and Gunther (1983) and Turner(1984)). This approach, while lending some insight to the mechanics of some simple pulse sequences, can lead to misunderstandings and wrong conclusions about the behaviour of the spin system. This approach completely fails to describe multiple quantum coherences. The density matrix treatment is the most complete description of the spin system that is possible. However, this treatment is not very transparent (or understandable to the uninitiated) and does not easily lead to an intuitive feel for the behavior of spins in NMR experiments. The product operator formalism is a short hand form of the density matrix description that keeps the correctness of the density matrix treatment, but at the same time, allows the experimentalist to retain a semblance of intuition.

#### 13.1 Coupled Spin Systems

A coupled spin system, IS, such as in a  $^{13}\text{C}$ - $^1\text{H}$  moiety, from the viewpoint of the  $^{13}\text{C}$  nucleus the sample can be described as a mixture of two different compounds, one with the attached  $^1\text{H}$  spin "up" and an almost equimolar amount of molecules with the attached  $^1\text{H}$  spin "down". This description is the one that is used to show the patterns of lines in a coupled spin system.

For  $^{13}\text{C}$  -  $^1\text{H}$  the species present are



Since there are (almost) equal numbers of  $\uparrow$  and  $\downarrow$  H spins, there are two  $^{13}\text{C}$  spectral lines of equal intensity. The frequency difference between the peaks is due to the local magnetic field of the coupled  $^1\text{H}$  spin, the  $\uparrow$  spin increases the magnetic field felt at the  $^{13}\text{C}$  nucleus and *vice versa*.

The spectrum looks (schematically) like:



For a C-H<sub>2</sub> moiety, We have one state with parallel <sup>1</sup>H spins up

$$^{13}\text{C} - \uparrow\uparrow, \quad (13.1.2)$$

two states with the <sup>1</sup>H spins aligned oppositely

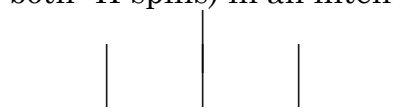
$$^{13}\text{C} - \uparrow\downarrow \downarrow\uparrow, \quad (13.1.3)$$

and

one state with parallel <sup>1</sup>H spins down.

$$^{13}\text{C} - \downarrow\downarrow. \quad (13.1.4)$$

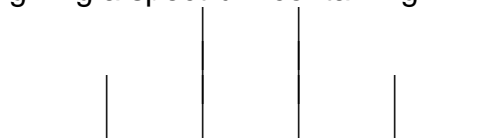
This gives a spectrum with three lines (assuming the same coupling constant for both <sup>1</sup>H spins) in an intensity ratio of 1:2:1.



Similarly, for a methyl group CH<sub>3</sub> the possible states are

$$\begin{aligned} ^{13}\text{C} - \uparrow\uparrow\uparrow \\ ^{13}\text{C} - \uparrow\uparrow\downarrow \uparrow\downarrow\uparrow \downarrow\uparrow\uparrow \\ ^{13}\text{C} - \downarrow\downarrow\uparrow \downarrow\uparrow\downarrow \uparrow\downarrow\downarrow \\ ^{13}\text{C} - \downarrow\downarrow\downarrow \end{aligned}$$

giving a spectrum containing 4 lines in a 1:3:3:1 intensity ratio.

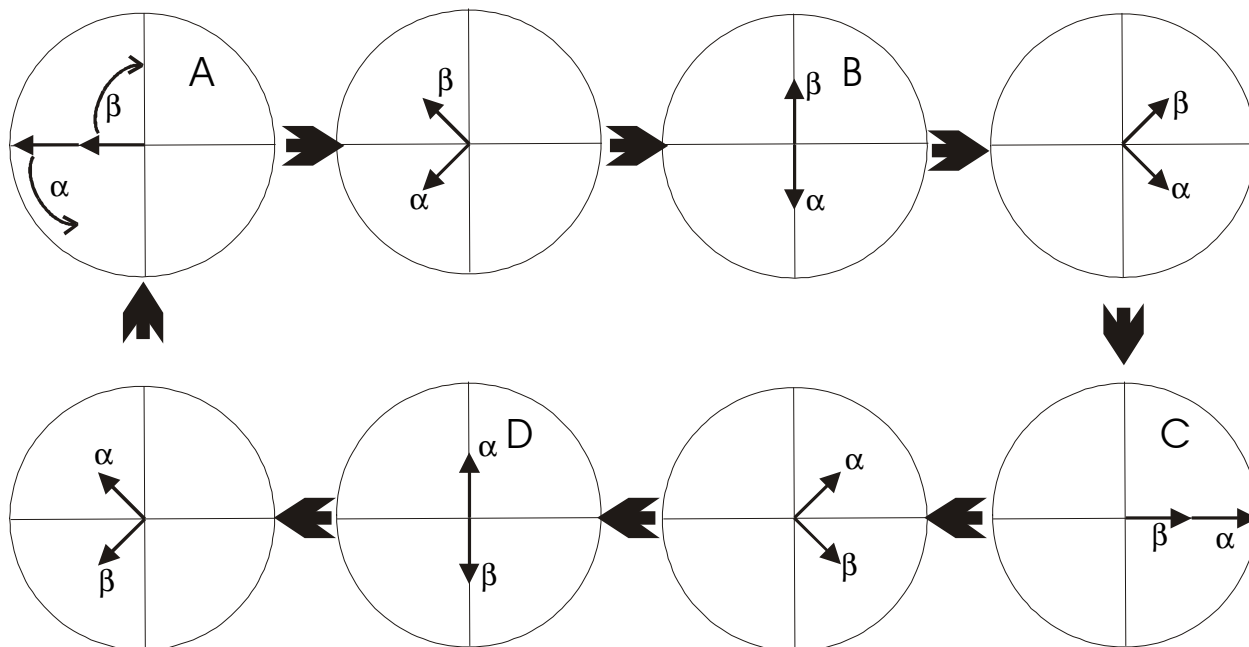


## 13.2 Semiclassical Picture of Coupling

Before embarking on the product operator description of coupling, it is useful to obtain an intuitive picture of coupling through a semi-classical approach. This approach was described by Lynden-Bell et al. Assume a heteronuclear spin system **I-S** with a non-zero scalar coupling between the two spins,  $J_{IS} \neq 0$ , e.g. the coupled <sup>1</sup>H<sup>13</sup>C in HC-Cl<sub>3</sub>. A 90° pulse (along the -X axis in this case) applied to the S<sub>z</sub> magnetization, generates transverse coherence S<sub>y</sub>.

$$\mathbf{S}_z \xrightarrow{-\pi/2 \hat{S}_x} \mathbf{S}_y \quad (13.2.1)$$

The state vector  $\mathbf{S}_y$  is composed of vectors from two very nearly equal populations of molecules: those coupled to  $\mathbf{I}$  spins in the  $\alpha$  state and those coupled to  $\mathbf{I}$  spins in the  $\beta$  state (Figure 13.2.1A). The local magnetic fields experienced by the  $\mathbf{S}$  spins in these two populations are slightly different because of the different fields of up and down  $\mathbf{I}$  spins. Therefore, the two types of  $\mathbf{S}$  spins precess at slightly different frequencies. In a proton-coupled  $^{13}\text{C}$  spectrum of chloroform, there are two resonance lines with the



**Figure 13.2.1** Evolution of semi-classical, coupled vectors.

frequency difference being the the coupling constant. If the  $\mathbf{S}$  spin is on resonance, *i.e.* the *decoupled*  $\mathbf{S}$  frequency is zero in the rotating frame, then the two  $\mathbf{S}_y$  vectors, which are attached to spin up and spin down  $\mathbf{I}$  spins, will precess apart at the coupling frequency. At time  $1/(2*J)$ , the two spin vectors will have precessed into opposite positions along the X coordinate axis (Figure 13.2.1B). As the spins continue to precess, the two vectors become parallel again along the -Y axis at a total time of  $1/J$  (Figure 13.2.1C). At a time of  $3/2J$ , the vectors will again be in opposite directions along the X axis. Note in (Figure 13.2.1D) that the  $\alpha$  and  $\beta$  spins are negative with respect to the positions in (Figure 13.2.1B). Finally, at a time  $2/J$  the spin vectors return to the -Y axis as in (Figure 13.2.1A).

The observed time domain signal is the sum of the two vectors that are precessing in the XY plane. When the vectors are aligned, a maximum signal will be observed. When the vectors are pointing in opposite directions, a zero signal will be observed. The observed signal due to the coupling is a cosine function, starting at a maximum, going through zero and a negative maximum, then returning through zero to the positive maximum. In this semi-classical picture, the observed magnetization vector

changes magnitude. It is not clear in this description "where the magnetization goes" when the observed signal is equal to zero.

### 13.3 Quantum Description - Antiphase Coherence

In analogy to the evolution of a spin vector evolving under chemical shift, we have

$$\mathbf{S}_y = \omega_s t \hat{s}_z \Rightarrow \mathbf{S}_y \cos \omega_s t - \mathbf{S}_x \sin \omega_s t. \quad (13.3.1)$$

We should be able to construct a similar relationship for evolution under coupling, e.g.

$$\mathbf{S}_y = J_{IS} \Rightarrow \mathbf{S}_y \cos \pi J_{IS} t - \mathbf{Q} \sin \pi J_{IS} t \quad (13.3.2)$$

Equation 13.3.2 represents the evolution of the coherence as the precession of a single vector, which does not change in magnitude, about an axis "J" in a plane with coordinate axes  $\mathbf{S}_y$  and  $\mathbf{Q}$ . What is the axis  $\mathbf{Q}$  and what is the axis  $\mathbf{J}$ ? A schematic of this concept is shown in Figure 13.3.1.

Again referring to a semi-classical picture of a coupled spin system, the two counter rotating components will evolve due to coupling from the Y axis to opposite directions along the X axis (Equation 13.3.3).

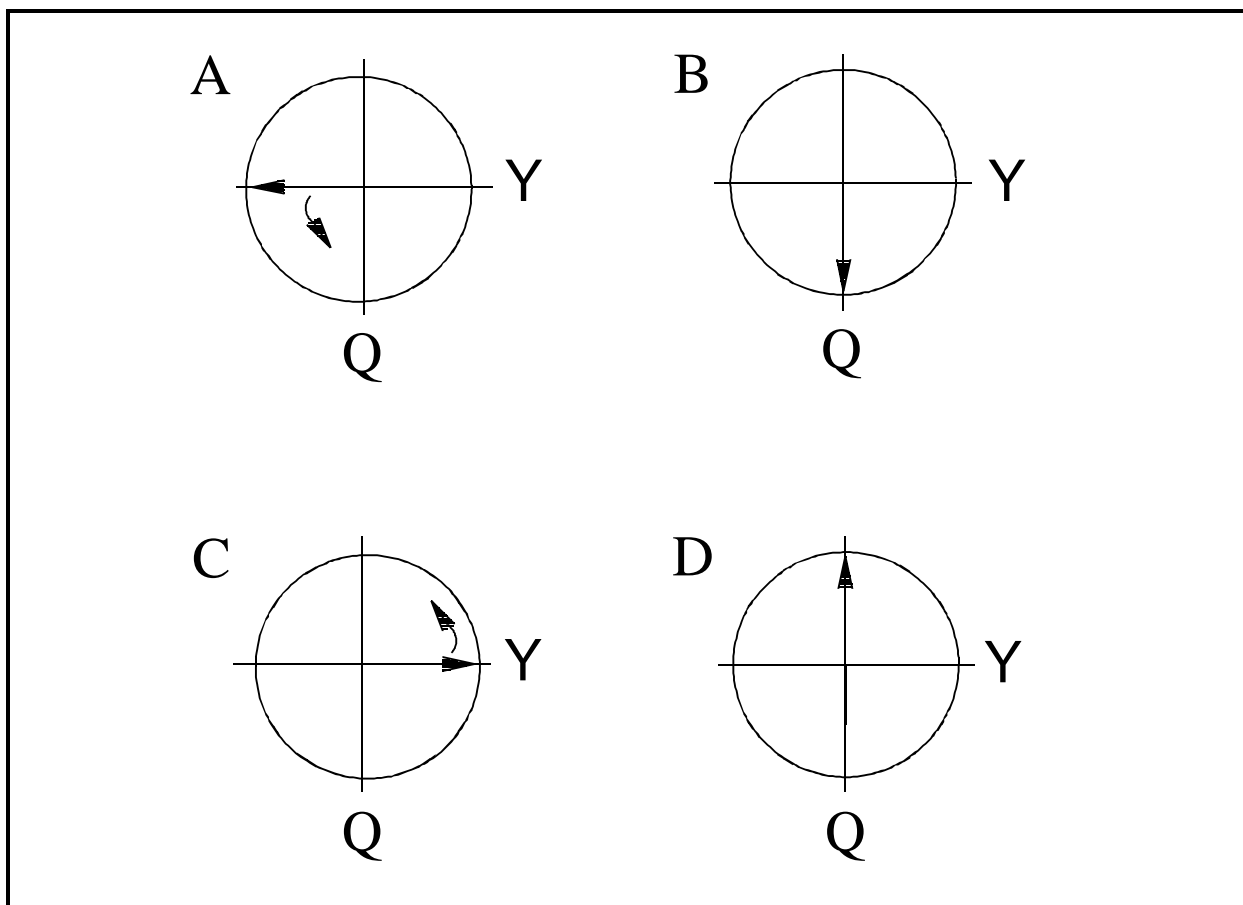
$$\alpha \mathbf{S}_y + \beta \mathbf{S}_y = (1/(2 \cdot J)) \Rightarrow -\alpha \mathbf{S}_x + \beta \mathbf{S}_x \quad (13.3.3)$$

The "amounts" of each of the components are given by the "concentration" of the attached up and down I spin,  $\alpha$  and  $\beta$ . The expression in Equation 13.3.3 can be rearranged to

$$-\alpha \mathbf{S}_x + \beta \mathbf{S}_x = (\alpha - \beta) \cdot -\mathbf{S}_x. \quad (13.3.4)$$

The quantity  $(\alpha - \beta)$  in Equation 13.3.4 is the population difference across the I energy levels and, therefore, is equivalent to the longitudinal magnetization of the coupled spin  $\mathbf{I}_z$ . More precisely,  $\alpha - \beta$  is proportional to the expectation value  $\mathbf{I}_z$ . By substituting  $\mathbf{I}_z$  for  $(\alpha - \beta)$  one obtains

$$(\alpha - \beta) \cdot -\mathbf{S}_x = \mathbf{I}_z \mathbf{S}_x. \quad (13.3.4)$$



**Figure 13.3.1.** Representation of a single vector representing evolution under scalar coupling. The rotation occurs about axis **J** coming out of the plane and the axis labeled **Q** is analogous to the semiclassical state where there opposite vectors cancel.

and the evolution in Equation 13.3.3 can be rewritten as

$$\mathbf{S}_y == (1/(2*J)) ==> -2\mathbf{I}_z\mathbf{S}_x \quad (13.3.5)$$

(NOTE: A normalizing factor of 2 has been introduced)

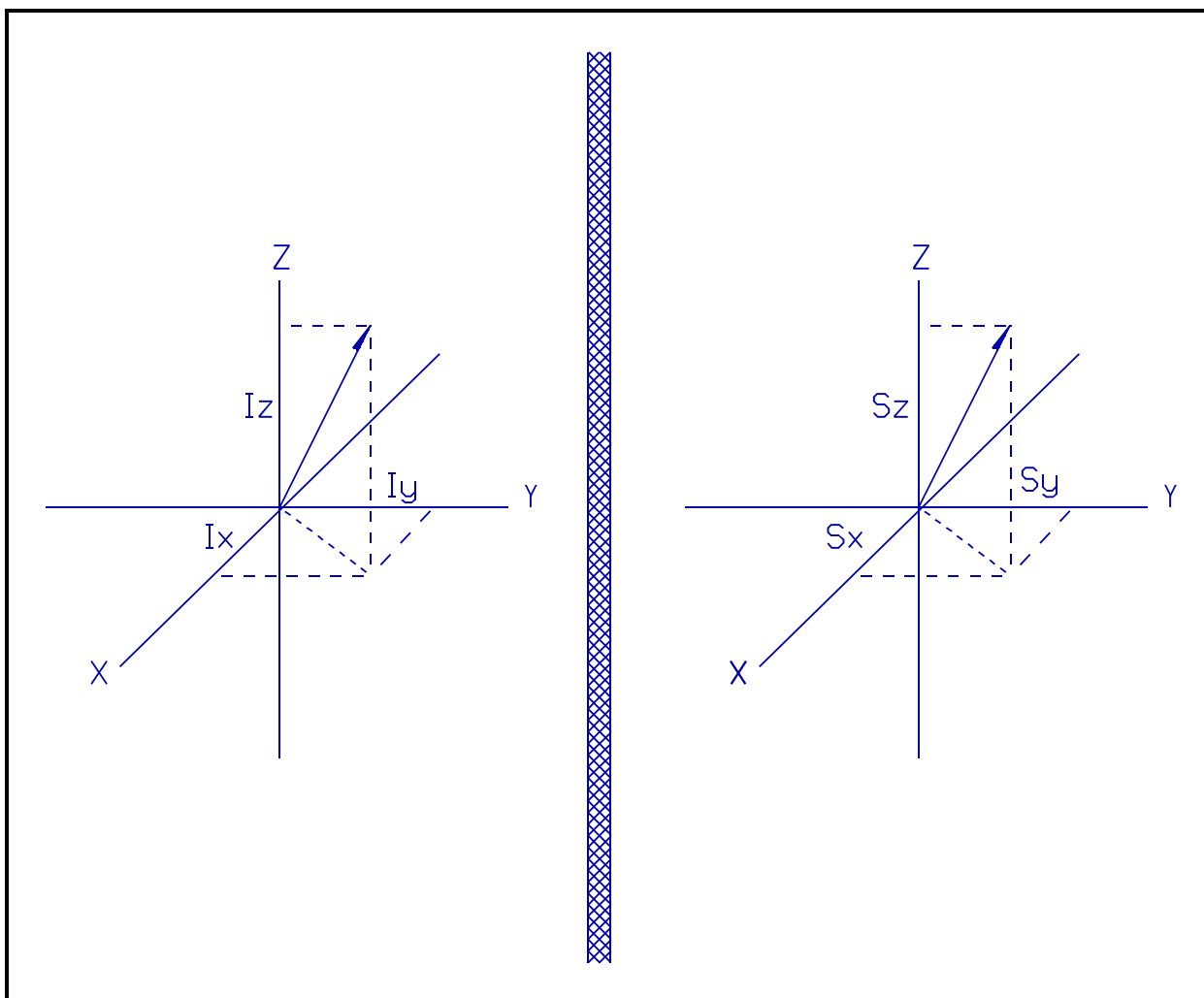
The  $-2\mathbf{I}_z\mathbf{S}_x$  state in Equation 13.3.5 is known as  $-\mathbf{S}_x$  magnetization that is antiphase with respect to **I**. This state is not directly observable under any experimental conditions, which is consistent with a picture involving the sum of oppositely pointed vectors. A more general term, *coherence*, is normally used in place of magnetization for the description of non-observable terms. The term coherence also can be accurately used to describe observable magnetization.

As described in Section 13.2, After arriving at the antiphase state in Equation 13.3.5, the two **S** vectors will again align along the  $-\mathbf{S}_y$  axis, and later form the positive antiphase state  $2\mathbf{I}_z\mathbf{S}_x$ , before completing a full cycle back to  $\mathbf{S}_y$ . The time dependence

can be written,

$$\mathbf{S}_y = \pi J_{IS} t \hat{I}_z \hat{S}_z \Rightarrow \mathbf{S}_y \cos(\pi J_{IS} t) - 2I_z \mathbf{S}_x \sin(\pi J_{IS} t) \quad (13.3.6)$$

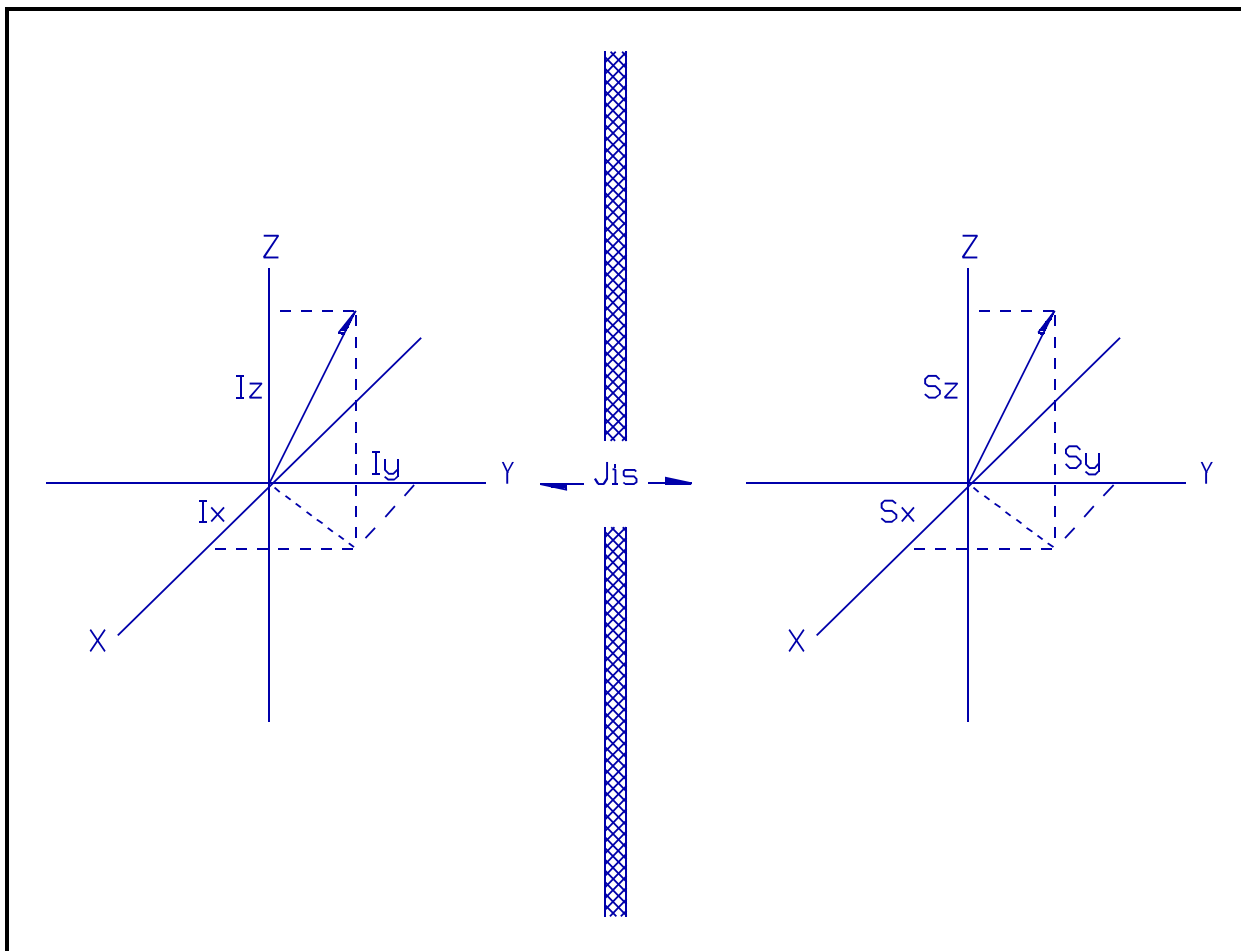
Transverse magnetization oscillates between inphase ( $\mathbf{S}_y$ ) and antiphase coherence ( $2I_z \mathbf{S}_x$ ). Note that the  $\mathbf{J}$  axis is replaced with the rotation operator  $2I_z \mathbf{S}_z$  for the coupling interaction. This operator arises from the form of the coupling interaction,  $\mathbf{J} \cdot \mathbf{S}$ , in the



**Figure 13.4.1.** Schematic representation of two "separate universes" and their coordinate systems. The wall between the two spaces signifies that there is no interaction between the systems.

Hamiltonian. The dot product of  $\mathbf{I}$  and  $\mathbf{S}$  is  $I_z S_z + I_x S_x + I_y S_y$ . In the weak coupling regime, where the difference in chemical shift between the two coupled spins is much greater than the coupling constant, the terms  $I_x S_x$  and  $I_y S_y$  are oscillatory and in time

average to zero. This leaves only the  $I_z S_z$  as the weak coupling term. This is not the case for strong coupling where the transverse terms are retained; the strong coupling interaction does not fundamentally alter the description of coupled spin systems, adding only unnecessary complications. We will assume the weak coupling condition in all cases except where noted.



**Figure 13.4.2.** Schematic representation of the universe of two coupled spins. The hole in the wall between the two spaces allows one spin to "see" what the other is "doing".

### 13.4 Two-Spin Space

Without introduction of scalar coupling or other interactions, a space of three dimensions is sufficient to describe the behavior of nuclear spins. Even if two different types of non-interacting spins are under study, each spin inhabits its own universe (space) described by a unique three dimensional coordinate system (See Figure 13.4.1). It seems natural to think of each separate spin space as a whole, ignoring the

other one. We can represent the state of the two spaces by the by two, three-dimensional vectors or by a single six-dimensional vector ( $\mathbf{I}_x, \mathbf{I}_y, \mathbf{I}_z, \mathbf{S}_x, \mathbf{S}_y, \mathbf{S}_z$ ). Although it seems natural to think of these as separate spaces, it is just as easy to think of it as a single six-dimensional space. The components of the vectors are obtained by projecting them onto the six, mutually-orthogonal, axes of this space. Perhaps it is not easy to grasp more than 3 dimensions in the minds-eye, but one can always envision three-dimensional sub-spaces of the higher dimensional space, *i.e.* since the axes are all orthogonal, any convenient set of three axis can be used to form a three-dimensional subspace.

The introduction of coupling into a two spin system is analogous to poking a hole in the wall that separates the two universes (Figure 1.4.2) thus allowing the spins to feel the motion of the other spin. To generate a space that contains two interacting spins,  $\mathbf{I}$  and  $\mathbf{S}$ , the x, y, and z operators for each spin must be represented, but also the interaction (*i.e.* coupling) of the spins must be represented. However, it appears that we don't have any axes to spare, since all of the axes are "in use" describing the x, y, and z components of the two individual spins. To extend the classical vector analogy to include the coupling interaction, there must exist another axis orthogonal from the two sets of three-dimensional cartesian coordinates.

### 13.5 Two Spin Product Operators

The terms that involve two operators (e.g.  $2\mathbf{I}_z\mathbf{S}_x$ ) are similar to  $\mathbf{S}_x, \mathbf{S}_y,$  and  $\mathbf{S}_z$  but describe coordinate axes that are in a space with more than three dimensions. In order to describe a spin system the "space" of the description must be large enough to hold all of the information necessary to completely define the system. For a single non-interacting spin the space consists of "operators" that correspond to the three spatial coordinate axes and an identity operator to complete the mathematical "group". A spin  $\mathbf{I}$  would have operators " $\mathbf{I}_x, \mathbf{I}_y, \mathbf{I}_z,$  and  $\mathbf{I}_E$ ". The three operators  $\mathbf{I}_x, \mathbf{I}_y,$  and  $\mathbf{I}_z$  are just the cartesian coordinates for the classical magnetization vector for spin  $\mathbf{I}$ . The  $\mathbf{I}_E$  operator can be thought of as the bulk of magnetic spins that have equal populations in the quantum mechanical energy levels and thus do not give rise to any net magnetization. The  $\mathbf{I}_E$  operator could also be used to described a saturated spin system, *i.e.* a system that has equal populations in both energy levels and no net magnetization.

The coordinates (axes) that are required to describe a coupled two spin system are generated by the "tensor products" of the  $\mathbf{I}$  and  $\mathbf{S}$  spin operators. In the product operator formalism the tensor products are obtained by taking all possible of the combinations of the  $\mathbf{I}$  and  $\mathbf{S}$  operators ( $\mathbf{I}_E, \mathbf{I}_x, \mathbf{I}_y, \mathbf{I}_z, \mathbf{S}_E, \mathbf{S}_x, \mathbf{S}_y, \mathbf{S}_z$ ).

Identity

$$\mathbf{I}_E * \mathbf{S}_E = \mathbf{E}$$



Single Quantum (Magnetic quantum number =  $\pm 1$ )

$$\begin{array}{ll} I_x * S_e = I_x & \text{SQ} \\ I_y * S_e = I_y & \text{SQ} \end{array} \quad \begin{array}{ll} I_e * S_y = S_y & \text{SQ} \\ I_e * S_x = S_x & \text{SQ} \end{array}$$

Anti-Phase Single Quantum (Magnetic quantum number =  $\pm 1$ )

$$\begin{array}{l} I_z * S_y = 2I_z S_y \\ I_y * S_z = 2I_y S_z \\ I_x * S_z = 2I_x S_z \\ I_z * S_x = 2I_z S_x \end{array}$$

Longitudinal Magnetization (Magnetic quantum number = 0)

$$I_z * S_e = I_z \quad \text{LM} \quad \quad I_e * S_z = S_z \quad \text{LM}$$

Longitudinal two spin order (Magnetic quantum number = 0)

$$I_z * S_z = 2I_z S_z$$

Two spin Multiple quantum (Magnetic quantum number =  $0, \pm 2$ )

$$\begin{array}{l} I_x * S_y = 2I_x S_y \\ I_y * S_y = 2I_y S_y \\ I_x * S_x = 2I_x S_x \\ I_y * S_x = 2I_y S_x \end{array}$$

NOTE: The 2 multiplier is a normalization constant. The constant is equal to  $2^{(\text{the number of operators} - 1)}$  in the product operator.

The only physically observable operators are  $I_x$ ,  $I_y$ ,  $S_x$ , and  $S_y$  corresponding to transverse magnetization that induces current in the receiver coil ( $I_z$  and  $S_z$  are also physically observable but are not measured directly by normal NMR techniques). The anti-phase single quantum terms are formally not observable, but can evolve through scalar coupling into observable terms during a "free precession" period in a pulse sequence and many times are the important terms in an experiment.

These "product operators" can be used to completely describe evolution of a weakly coupled two spin system during an arbitrary pulse sequence. The 16 product operators that are generated by this procedure can be viewed as the **E** operator and the 15 coordinate axes that are necessary to describe an arbitrary state of the two interacting spins. Having more than three dimensions may seem difficult to comprehend, but it is no more difficult than having a series of experiments with coordinates (pH, temperature,

ionic strength, concentration, E. coli mutant) that span a 5 dimensional vector space. The extension of the product operator formalism to larger spin systems is straight forward.

The behaviour of the  $I^*S$  product operators with respect to pulses and chemical shifts are as if the  $I$  and  $S$  spins are independent. A rotation of one spin does not effect the other spin even in a state with more than one operator.

Pulses:

Non-selective pulse, where both spins are pulsed. Here the spins are rotated with different phases

$$2I_xS_z \xrightarrow{\pi/2\hat{I}_x + \pi/2\hat{S}_y} 2I_xS_x$$

Spin selective pulse, where only one spin is pulsed.

$$2I_xS_z \xrightarrow{\pi/2\hat{I}_y} -2I_xS_z$$

Pulses operating on one spin do not affect the other spin(s).

$$2I_zS_x \xrightarrow{\pi/4\hat{I}_y + \pi/6\hat{S}_y} 2[I_z \cos \pi/4 + I_x \sin \pi/4] \\ * [S_x \cos \pi/6 - S_z \sin \pi/6]$$

Chemical shifts:

$$-I_y \xrightarrow{\omega_I \hat{I}_z} -I_y \cos \omega_I t + I_x \sin \omega_I t$$

$$2I_xS_z \xrightarrow{\omega_I \hat{I}_z + \omega_S \hat{S}_z} 2[I_x \cos \omega_I t + I_y \sin \omega_I t] S_z \\ \equiv 2I_xS_z \cos \omega_I t + 2I_yS_z \sin \omega_I t$$

$$2I_zS_z \xrightarrow{\omega_I \hat{I}_z + \omega_S \hat{S}_z} 2I_zS_z$$

$$2I_xS_y \xrightarrow{\omega_I \hat{I}_z + \omega_S \hat{S}_z} 2[I_x \cos \omega_I t + I_y \sin \omega_I t] \\ * [S_y \cos \omega_S t - S_x \sin \omega_S t] \\ \equiv 2I_xS_y \cos \omega_I t \cos \omega_S t \\ - 2I_xS_x \cos \omega_I t \sin \omega_S t \\ + 2I_yS_y \sin \omega_I t \cos \omega_S t \\ - 2I_yS_x \sin \omega_I t \sin \omega_S t$$

Scalar coupling:

$$I_x \xrightarrow{\pi J_{IS} \hat{I}_z \hat{S}_z} I_x \cos \pi J_{IS} t + 2I_yS_z \sin \pi J_{IS} t$$

$$I_z = \pi J_{IS} t \hat{I}_z \hat{S}_z \Rightarrow I_z$$

$$2I_z S_x = \pi J_{IS} t \hat{I}_z \hat{S}_z \Rightarrow 2I_z S_x \cos(\pi J_{IS} t) + S_y \sin(\pi J_{IS} t)$$

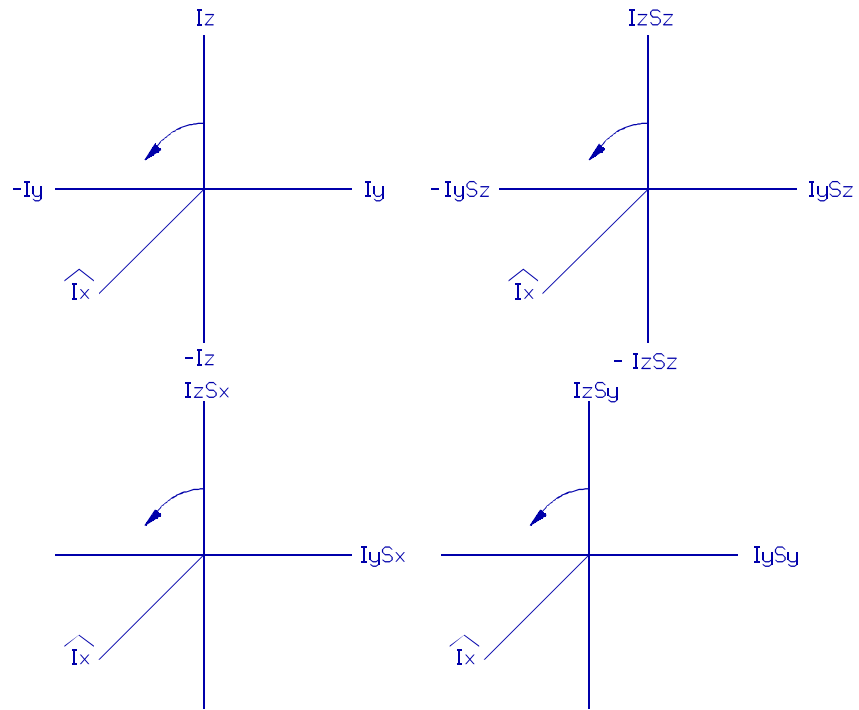
$$2I_x S_y = \pi J_{IS} t \hat{I}_z \hat{S}_z \Rightarrow 2I_x S_y \text{ (no rotation if no passive coupling partner)}$$

In a **IST** spin system with **IT** coupling:

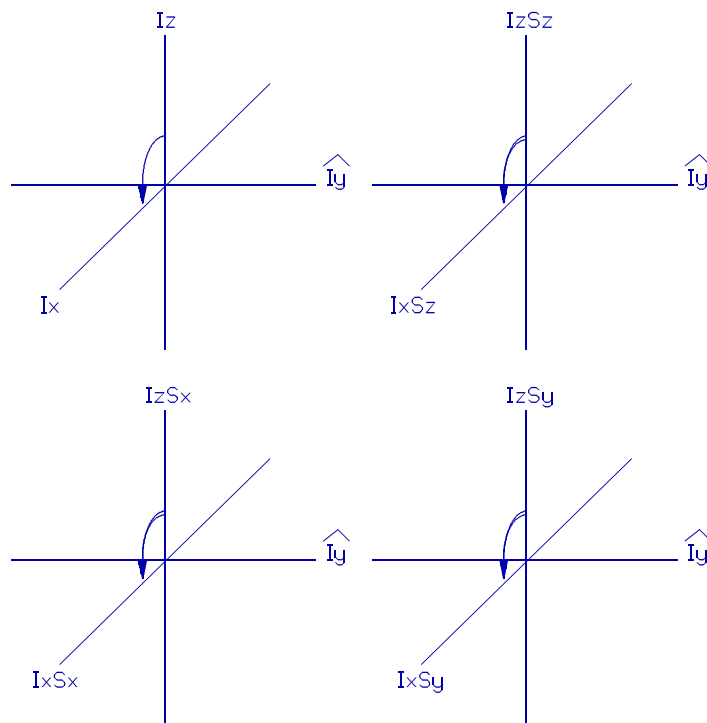
$$2I_x S_y = \pi J_{IT} t \hat{I}_z \hat{T}_z \Rightarrow 2I_x S_y \cos(\pi J_{IT} t) + 2I_y S_y T_z \sin(\pi J_{IT} t)$$

The following are the most common three dimensional subspaces for a coupled two spin system. They are collected as rotations about a given axis, *i. e.* the first figure shows rotations about the X axis for the **I** spin. Only the **I** spin rotations are shown, the **S** rotations can be obtained by exchanging **S** for **I** in all cases except for coupling where the diagram remains the same.

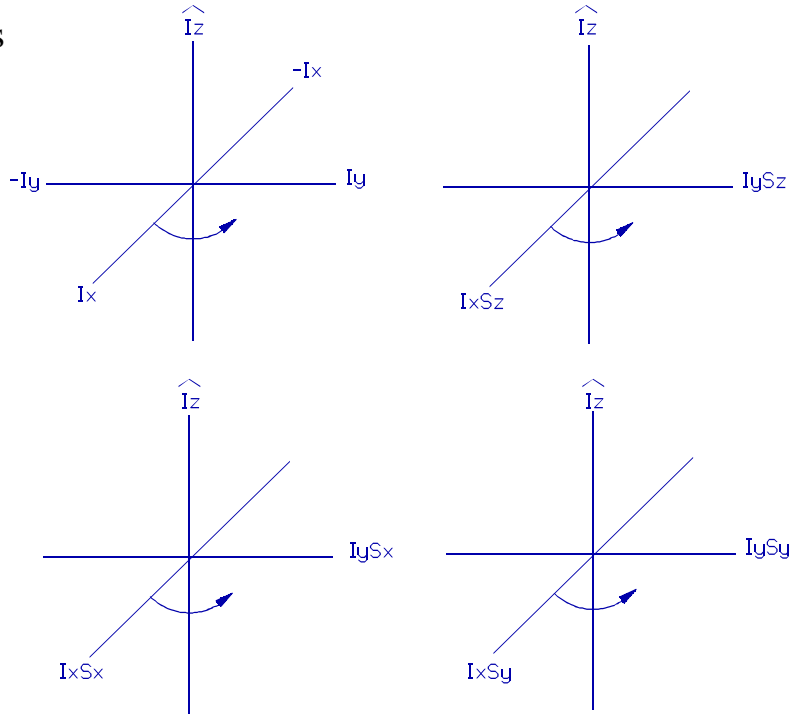
### X axis



### Y axis



Z axis



Coupling  
( $I_S$ )  
 $Z'Z'$

