

# ***A Pictorial Operator Formalism for NMR Coherence Phenomena***

**Po-Kang Wang and Charles P. Slichter**

**Department of Physics and Materials Research Laboratory  
University of Illinois at Urbana-Champaign  
Urbana, Illinois 61801**

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## ***I. INTRODUCTION***

An NMR pulse experiment can often be more easily understood if it is described in a pictorial manner. In classical models spins are visualized as vectors, rotated by an alternating magnetic field during r.f. pulses, and between pulses, precessing at frequencies corresponding to each spin's local magnetic field. There are however many important phenomena such as multiquantum coherence, coherence transfer, dipolar order, and solid echoes, which are more difficult to describe using classical models (1,2). In this paper we describe an operator formalism which we have found useful both to show how different pulse sequences work, and to bring out how they are related to one another. The method was developed in the thesis of one of us (PKW) in the course of our work on adsorbed molecules on metal surfaces (3). When

we considered publication, we discovered that in the meanwhile a substantial article by Sorensen et al appeared, which gave a complete and general treatment of the method (4a). They have called the method "Product Operator Formalism". In addition, a clear discussion of the formal method for two spins by Van der Ven and Hilbers (4b) has also appeared which represents a very systematic approach and treats as an example the 2D correlated experiment for two like nuclei coupled to each other, but with a chemical shift difference. Though both papers provide a clear, mathematically precise treatment of the topic, we decided that some readers might still find useful a short article, tutorial in nature, aimed at highlighting the similarities and the differences between the several coherence phenomena. By treating a very simple system of two spin-1/2 nuclei, we hope to show the relationship among a

number of experiments, the pictorial nature of the method, and its potential usefulness as an aid in designing pulse sequences.

We consider a system of two spin-1/2 nuclei with a Zeeman interaction,

$$H_0 = -\hbar H_0(\gamma_1 I_{1z} + \gamma_2 I_{2z}) \quad (1)$$

and a spin-spin coupling,

$$H_C = \hbar a I_{1z} I_{2z} \quad (2)$$

The Zeeman coupling can represent unlike spins ( $\gamma_1 \neq \gamma_2$ ) or like spins ( $\gamma_1 = \gamma_2$ ). The spin-spin coupling can represent an approximation to the J-coupling,

$$\hbar a \hat{I}_1 \cdot \hat{I}_2 \quad (3)$$

or to the dipolar coupling,

$$(\hbar a)(I_{1z} I_{2z} - \frac{1}{2} I_{1x} I_{2x} - \frac{1}{2} I_{1y} I_{2y}) \quad (4)$$

of (1) unlike spins, and (2) like spins if they have a chemical shift difference much larger than the coupling.

The spin-spin coupling in eqn. 2 is also exact for the dipolar coupling of like spins with zero chemical shift difference provided one redefines the coupling strength. In this case the total spin angular momentum of the pair,  $I$ , is an eigenvalue, and the spins form a triplet ( $I=1$ ) and a singlet ( $I=0$ ). Since the r.f. field does not mix the triplet states with the singlet state, and the singlet state contributes no magnetization, one can keep only the triplet states, and consider the system as  $I=1$ . One can write the dipolar coupling as

$$(\hbar 3a/2)(I_{1z} I_{2z} - \frac{1}{3} \hat{I}_1 \cdot \hat{I}_2) \quad (5)$$

The  $\hat{I}_1 \cdot \hat{I}_2$  term is a constant (1/4) for the triplet states, and can be dropped from the Hamiltonian. We then have again the coupling as in eqn. 2 except that "a" should be replaced by "3a/2".

We are not going to include the chemical shift or field inhomogeneity in the Hamiltonian, since they do not significantly change the results, but make the calculation much more cumbersome.

Actually, if one includes chemical shifts and field inhomogeneity, their effects typically disappear if one produces a spin echo. (In the appendix, we treat a frequency off-set effect as part of the multiple quantum coherence experiment.)

In Section II we present the basic theoretical model. In Section III we apply it to show how to generate and detect multiple quantum coherence. In Section IV we apply the method to explain the famous Jeener-Broekaert pulse sequence for converting Zeeman order to dipolar order. We treat the Powles-Mansfield solid echo in Section V. In Section VI we discuss the method Maudsley and Ernst of producing heteronuclear coherence transfer. In the appendix, we explain the frequency offset used in connection with n-quantum coherence to distinguish spectra by n-values.

## II. CLASSICAL PICTURES AND THE OPERATOR FORMALISM

Since most experiments start with a Free Induction Decay, we will use the description of a FID to illustrate the similarities and differences between the classical pictures and the quantum-mechanical operator formalism. In both methods one first transforms the system from the laboratory frame to the rotating frame, in which the alternating field becomes stationary. If the r.f. is on resonance, the effect of the static field disappears, leaving only the coupling to the r.f. field and the spin-spin coupling. If the former is much larger than the latter, during r.f. pulses the spins will precess about the r.f. field  $H_1$  (along the x-axis). The net effect of r.f. pulses thus becomes that of rotations.

At thermal equilibrium both spins lie along the z-axis. If one rotates the first spin by a 90° pulse to lie along the y-axis, the classical picture states that, following the pulse, the spin precesses in the local field produced by its neighbor. The angle of precession after a time  $t$  is  $at/2$ , clockwise or counterclockwise in the rotating frame depending on whether the neighbor is pointing up or down. There is therefore an oscillatory net magnetization of the first spin along the y-axis:

$$M_{1y} = M_{10} \cos (at/2) \quad (6)$$

Does the result hold for  $M_{1y}$  if instead of just the first spin, *both* spins are rotated by a pulse, and as a result each spin's neighbor is neither pointing up nor down? The answer is yes, but we need to use a quantum mechanical description to derive the result unambiguously. Besides confirming the result in eqn. 6, the quantum mechanical result can also be presented in such a pictorial form that one can see clearly what additional pulses are needed to generate multiquantum coherence, dipolar echoes, solid echoes, coherence transfer, and so on.

Let us first describe the system at thermal equilibrium. In the high temperature approximation the state of the system can be described by a density matrix (5),

$$\rho = \frac{e^{-H/k_b T}}{\text{Tr } e^{-H/k_b T}} \approx 1/4 - H/4k_b T \quad (7)$$

The first term, as a constant, has no physical significance, and can be omitted. Since the Zeeman energy usually is much larger than the spin-spin coupling, the second term can be approximated by  $-H_0/4k_b T$ . For convenience we will omit the constant of proportionality, consider like spins and describe the density matrix at thermal equilibrium as simply

$$\rho(0) = I_{1z} + I_{2z} \quad (8)$$

(For unlike spins we include the  $\gamma$ 's in  $\rho(0)$ ).

We now want to consider the effect of an r.f. field, and subsequently the effect of the spin-spin coupling on the development of the density matrix with time. We follow the usual procedure of dividing the Hamiltonian into two terms,

$$H = H_0 + H_C \quad (9)$$

where  $H_0$  is the Zeeman energy and  $H_C$  contains the spin-spin coupling and the coupling to the r.f. field expressed in the laboratory frame. (While we do not explicitly treat chemical shift effects, they would also be included in  $H_C$ ). Then we transform

$\rho_L$ , the density matrix in the laboratory frame, to  $\rho$ , the density matrix in a convenient representation using the unitary operator  $S$

$$\rho(t) = S^{-1}(t) \rho_L S(t) \quad (10)$$

If  $S = \exp(-iH_0 t/\hbar)$  we speak of a transformation to the interaction representation. If  $S = \exp(i\omega t I_z)$  we speak of a transformation to the rotating frame (rotating at frequency  $\omega$  in the same sense as the precession). If we tune exactly to resonance ( $\omega = \gamma H_0$ ) the two transformations are identical.  $\rho$  obeys the equation

$$d\rho/dt = \frac{i}{\hbar} [\rho, H_C^*] \quad (11)$$

where  $H_C^*(t) = S^{-1}(t)H_C S(t)$  is the sum of spin-spin coupling ( $\hbar a I_{1z} I_{2z}$ ) and coupling to the r.f. field in the rotating frame ( $-\hbar \gamma I_x H_1$ ).

Experimentally, we observe the transverse components of magnetization. If  $I_x$  and  $I_y$  are the components of total spin angular momentum along transverse axes in the rotating frame, we observe

$$\langle I_x \rangle = \text{Tr}\{I_x \rho\}$$

and (12)

$$\langle I_y \rangle = \text{Tr}\{I_y \rho\}$$

During a time interval in which  $H_C^*$  is independent of time, the solution of eqn. 11 is

$$\rho(t) = \exp(-iH_C^* t/\hbar) \rho(0) \exp(iH_C^* t/\hbar) \quad (13)$$

In the absence of r.f. pulses  $H_C^*$  consists only of the spin-spin coupling. During the r.f. pulses we assume the r.f. field strength is so great that we can neglect the spin-spin coupling. For  $H_1$  directed along the plus x-axis in the rotating frame, we denote a  $90^\circ$  pulse by " $90^\circ_x$ ". (Note that our definition of a  $90^\circ_x$  pulse is actually a  $-90^\circ$  rotation about the x-axis since this is the sense of

rotation of a spin with positive  $\alpha$ ).

Using  $\rho(0)$  in eqn. 8, the density matrix immediately after the pulse,  $\rho(0^+)$ , is given by

$$\rho(0^+) = \exp(i\pi I_x/2)(I_{1z} + I_{2z})\exp(-i\pi I_x/2) \quad (14)$$

using the well known operator relationship (6)

$$\exp(-i\phi I_z) I_x \exp(i\phi I_z) = I_x \cos\phi + I_y \sin\phi \quad (15)$$

and its cyclic permutations, eqn. 14 leads to

$$\rho(0^+) = I_{1y} + I_{2y} \quad (16)$$

Although one gets from eqn. 14 to eqn. 16 by operator manipulation, once one has been through the steps one realizes the result is equivalent to that of the classical picture. In this case a  $90_x^\circ$  pulse rotates  $I_{1z}$  to  $I_{1y}$ , and  $I_{2z}$  to  $I_{2y}$ .

We now want to consider the effect of the spin-spin coupling on the evolution of  $\rho$  after the pulse. Using eqn. 13 one has

$$\rho(t) = \exp(-iaI_{1z}I_{2z}t) (I_{1y} + I_{2y}) \exp(iaI_{1z}I_{2z}t) \quad (17)$$

The evolution of the two spins can now be considered separately. Making use of the result of eqn. 15, the evolution of  $I_{1y}$  is similar to a rotation about the z-axis by an angle of  $aI_{2z}t$ , i.e.,

$$\exp(-iaI_{1z}I_{2z}t) I_{1y} \exp(iaI_{1z}I_{2z}t) = I_{1y} \cos(aI_{2z}t) - I_{1x} \sin(aI_{2z}t) \quad (18)$$

where the meaning of cos and sin functions whose arguments include an operator defined by their series expansions:

$$\begin{aligned} \cos(aI_{2z}t) &= 1 - (aI_{2z}t)^2/2! + \dots \\ \sin(aI_{2z}t) &= aI_{2z}t - (aI_{2z}t)^3/3! + \dots \end{aligned} \quad (19)$$

For a spin 1/2 nucleus, we represent the spin operator  $I_\alpha$  ( $\alpha = x, y$  or  $z$ ) as  $\sigma_\alpha/2$ , with  $\sigma_\alpha$

being Pauli's matrices. Using the property of Pauli's matrices that  $\sigma_\alpha^2$  is equal to 1, we find that  $I_\alpha^2$  is equal to 1/4 for a spin-1/2 nucleus.

Alternatively the result can be derived from the following reasoning. The most general wavefunction of a spin-1/2 nucleus is a linear combination of the spin-up and spin-down states. Since both states are eigenfunctions of  $I_z^2$  with eigenvalue 1/4, the wavefunction is also an eigenfunction of  $I_z^2$  with eigenvalue 1/4. We can therefore replace the operator  $I_z^2$  with 1/4 for a spin-1/2 nucleus. Eqn. 19 can now be greatly simplified, and eqn. 18 becomes

$$\begin{aligned} \exp(-iaI_{1z}I_{2z}t) I_{1y} \exp(iaI_{1z}I_{2z}t) = \\ I_{1y} \cos(at/2) - 2I_{1x}I_{2z} \sin(at/2) \end{aligned} \quad (20)$$

If  $I_{2z}$  is replaced by  $\pm 1/2$ , eqn. 20 becomes identical to the classical description:  $\hat{I}_1$  precesses in the local field produced by  $\hat{I}_2$ , clockwise or counterclockwise depending on whether  $\hat{I}_2$  is pointing up ( $I_{2z} = 1/2$ ) or down ( $I_{2z} = -1/2$ ). We can now include the evolution of  $I_{2y}$  in eqn. 20 and obtain

$$\rho(t) = I_{1y} \cos(at/2) - 2(I_{1x}I_{2z} + I_{2x}I_{1z}) \sin(at/2) \quad (21)$$

Using eqn. 12, we find that the first term in eqn. 21 gives the familiar oscillatory transverse magnetization

$$\langle I_y \rangle = \text{Tr}\{\rho(t) I_y\} = 2 \cos(at/2) \quad (22)$$

as does the classical picture. The second term in eqn. 21 gives no observable magnetization since it gives zero when the trace is computed. Nevertheless, it contains the essentials for a rich variety of coherence phenomena. With a properly selected second pulse, the term containing  $I_{1x}I_{2z}$  and  $I_{2x}I_{1z}$  can be transformed by rotations to give rise to two-quantum coherence, dipolar order, a solid echo, or coherence transfer, and then the result inspected by application of further pulses.

Before we go on with each of these phenomena, let us summarize the operator formalism we have just described.

1) Since the Pauli's matrices  $\{1, \sigma_\alpha\}$  constitute a complete set of bases for a spin 1/2 system, and the product  $\{1, \sigma_{1\alpha}\} \times \{1, \sigma_{1\alpha}\}$  a complete set for a two-spin-1/2 system, the density matrix of two spin-1/2 nuclei can always be expressed as a linear combination of  $1, I_{1\alpha}, I_{2\beta},$  and  $I_{1\alpha} I_{2\beta}$ . The extension can be easily made for any number of spin-1/2 nuclei. This is the origin of the name "Product Operator Formalism".

2) The effect of r.f. pulses is simply that of rotations, as in the classical pictures. The effect of a rotation operator  $\mathbf{R}$  on  $I_{1\alpha} I_{2\beta}$  can be obtained as

$$\mathbf{R}^{-1}(I_{1\alpha} I_{2\beta})\mathbf{R} = (\mathbf{R}^{-1} I_{1\alpha} \mathbf{R})(\mathbf{R}^{-1} I_{2\beta} \mathbf{R}) \quad (23)$$

3) Between pulses the effect of the spin-spin coupling on the evolution of  $I_{1y}$  is given by eqn. 20. If one denotes the evolution,  $\exp(i a I_{1z} I_{2z} t)$ , by  $\mathbf{T}$ , then the evolution of the first spin is given by

$$\begin{aligned} \mathbf{T}^{-1} I_{1y} \mathbf{T} &= I_{1y} \cos(at/2) - 2 I_{1x} I_{2z} \sin(at/2) \\ \mathbf{T}^{-1} I_{1x} \mathbf{T} &= I_{1x} \cos(at/2) + 2 I_{1y} I_{2z} \sin(at/2) \end{aligned} \quad (24)$$

Similarly one can write down the evolution for the second spin. The evolution of  $I_{1\alpha} I_{2\beta}$  is then given by

$$\mathbf{T}^{-1}(I_{1\alpha} I_{2\beta})\mathbf{T} = (\mathbf{T}^{-1} I_{1\alpha} \mathbf{T})(\mathbf{T}^{-1} I_{2\beta} \mathbf{T}) \quad (25)$$

Using these results we are now ready to describe any pulse sequence.

### III. MULTIQUANTUM COHERENCE

The excitation of 2-quantum coherence by pulse techniques was first demonstrated by Hatanaka, Terao, and Hashi and by Hatanaka and Hashi (7). Since then the technique has been developed into a

sophisticated tool in the analysis of high resolution spectroscopy in the laboratories of Pines, Ernst, the Volds, Freeman and many other researchers (8-11). Roughly speaking 2-quantum coherence involves flipping two spins simultaneously via the coupling between them, and 3-quantum coherence involves flipping three spins. For the system of two spin-1/2 nuclei, 2-quantum coherence is represented by density matrix elements connecting the state with both spins pointing up and the state with both spins pointing down, a so-called  $\Delta m = \pm 2$  matrix element (where  $m = m_1 + m_2$  is the sum of the eigenvalues of  $I_{1z}$  and  $I_{2z}$ ). One is therefore looking for terms like  $I_{1x} I_{2x}, I_{1x} I_{2y}, I_{1y} I_{2x},$  or  $I_{1y} I_{2y}$  in the density matrix. We say that these terms contain 2-quantum coherence (they also include some  $\Delta m = 0$  terms).

It is necessary to consider three problems in connection with multiple quantum coherence: (1) how does one generate the terms in  $\rho$  which give rise to the appropriate matrix elements of  $\rho$  (such as the  $\Delta m = \pm 2$  terms of  $\rho$  for 2-quantum coherence). (2) Since as we shall see the transverse component of magnetization arises solely from 1-quantum coherence, how can higher order coherence be revealed? (3) How can one distinguish the various orders of coherence?

We will treat the first and second topics in the text, and discuss the third topic in the appendix.

Let us examine the density matrix after a  $90_x^\circ$  pulse and an evolution time  $t$  (eqn. 21). The terms  $I_{1x} I_{2z}$  and  $I_{2x} I_{1z}$  connect  $\Delta m = \pm 1$  states, hence do not give 2-quantum coherence. The question is can we find a pulse (or pulses) which will convert  $\Delta m = \pm 1$  terms into  $\Delta m = \pm 2$  terms? Utilizing the fact that  $\langle m_1 m_2 | I_{1\alpha} I_{2\beta} | m_1' m_2' \rangle = \langle m_1 | I_{1\alpha} | m_1' \rangle \times \langle m_2 | I_{2\beta} | m_2' \rangle$  we realize that it is the  $I_{1z}$  and  $I_{2z}$  terms which we must change. Thus, formally we must find rotation operator  $\mathbf{R}$  such that

$$\begin{aligned} \mathbf{R}^{-1} I_{1x} I_{2z} \mathbf{R} &= I_{1x} I_{2x} \\ \text{or} \quad I_{1x} I_{2y} \text{ or } I_{1y} I_{2x}, \text{ or } I_{1y} I_{2y} \end{aligned} \quad (26)$$

or some linear combination of these.

Since  $\mathbf{R}^{-1} I_{1x} I_{2z} \mathbf{R} = (\mathbf{R}^{-1} I_{1x} \mathbf{R})(\mathbf{R}^{-1} I_{2z} \mathbf{R})$  we immediately see that a  $90_x^\circ$  pulse which produces

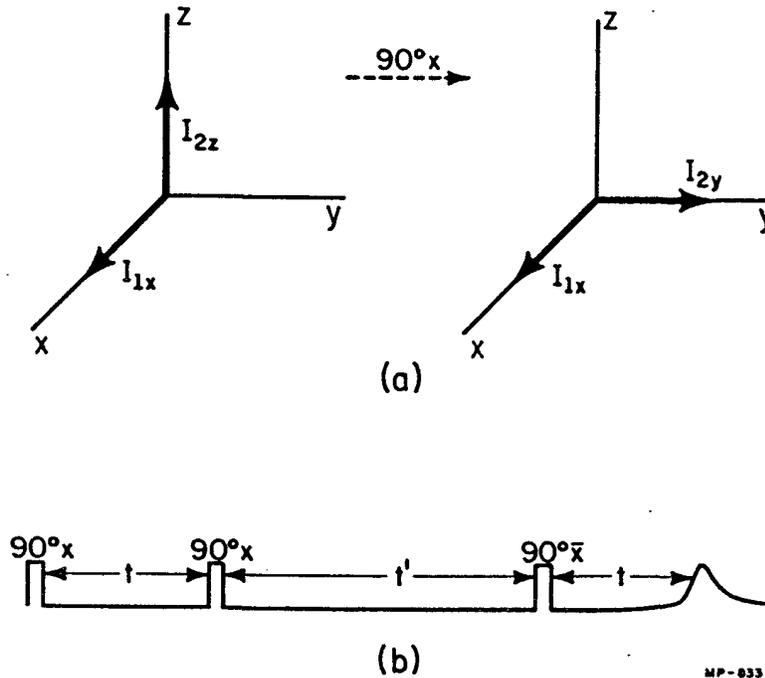


Figure 1. a)  $I_{1x}I_{2z}$  is rotated by a  $90^\circ_x$  pulse to  $I_{1x}I_{2y}$ , which contains 2-quantum coherence. b) A simple pulse sequence for multiquantum coherence experiments.

a rotation of ( $-90^\circ$ ) about the x-axis will leave  $I_{1x}$  alone, but convert  $I_{2z}$  to  $I_{2y}$  (see Figure 1a).

Thus

$$\mathbf{R}^{-1}I_{1x}I_{2z}\mathbf{R} = I_{1x}I_{2y} \quad (27)$$

where  $\mathbf{R} = \exp(-i\pi I_x/2)$ . After the pulse the density matrix is

$$\begin{aligned} \rho(t^+) &= -I_z \cos(at/2) - 2(I_{1x}I_{2y} + I_{2x}I_{1y}) \sin(at/2) \\ &= -I_z \cos(at/2) + i(I_1^+ I_2^+ + I_1^- I_2^-) \sin(at/2) \end{aligned} \quad (28)$$

with the second term containing 2-quantum coherence.

Multiquantum coherence, however, cannot be directly observed as transverse magnetization since it contributes zero to  $\text{Tr}(I_x\rho)$  or  $\text{Tr}(I_y\rho)$ . One therefore has to transfer multiquantum coherence back to 1-quantum coherence for inspection. To convert the 2-quantum terms ( $I_{1x}I_{2y} + I_{2x}I_{1y}$ ) to 1-quantum coherence, we must convert one of the spin factors to a z-component  $I_{1z}$  or  $I_{2z}$ . An easy way to do so is to apply a  $90^\circ_{-x}$  pulse ( $H_1$  along -x axis), which brings the 2-quantum terms in the density matrix back to

$$\rho_{2q}(t^{++}) = -2(I_{1x}I_{2z} + I_{2x}I_{1z}) \sin(at/2). \quad (29)$$

Using eqn. 24 and eqn. 25, and the fact that  $I_z^2$  equals 1/4, one obtains the density matrix at the time of the stimulated echo as

$$\rho_{2q}(2t) = -2(I_{1x}I_{2z} + I_{2x}I_{1z})\sin(at/2) \cos(at/2) - I_y \sin^2(at/2) \quad (30)$$

Since only the last term of eqn. 30 gives a non-vanishing signal  $M_y$ , the signal which goes through 2-quantum coherence has a t-dependence of  $\sin^2(at/2)$ . The signal from 2-quantum coherence therefore reaches its maximum when the pulse separation t is equal to  $\pi/a$ . In general, to generate multiquantum coherence, the time interval t has to be long enough for spins with their neighboring spins pointing in opposite directions to accumulate significant phase difference during the time interval t, i.e.

$$at \geq 1 \quad (31)$$

One of the most interesting uses of multiquantum coherence is to count spins in solids or on surfaces, for example to distinguish isolated protons as in a CH group, from proton pairs, as in a  $\text{CH}_2$  group (12). Then "a" arises from the nuclear dipole-dipole coupling. However, two CH groups in nearby molecules are in some sense a pair, as are the two protons on the opposite ends of the molecule HCCH. When should we say the two protons are single, when should we treat them as a pair? Eqn. 31 shows that if the proton-proton dipolar coupling strength, a, is very weak, as it would be for protons far apart in different molecules, it would take a long time, t, for the double quantum coherence to build up. However if the two protons are close, as they are in a  $\text{CH}_2$  group, a shorter time, t, will suffice.

What we must do, therefore, is to define the H-H distance which we call the "pair separation". Any protons which are that distance apart we call a pair. We use that coupling "a" to determine a time, t, needed to establish 2-quantum coherence, and inspect the strength of 2-quantum signals produced in that time. For protons farther apart, the 2-quantum coherence will not have time to build up, so they can only give 1-quantum coherence, i.e. a conventional resonance. Note that we can in this way search in an unknown system

for pairs such as in an HCCH (acetylene) molecule *provided* only that those molecules represent the only statistically common way in the sample that two protons can be this close to each other. This is the method employed by the authors in their study of the structure of acetylene adsorbed on Pt surfaces (1,12).

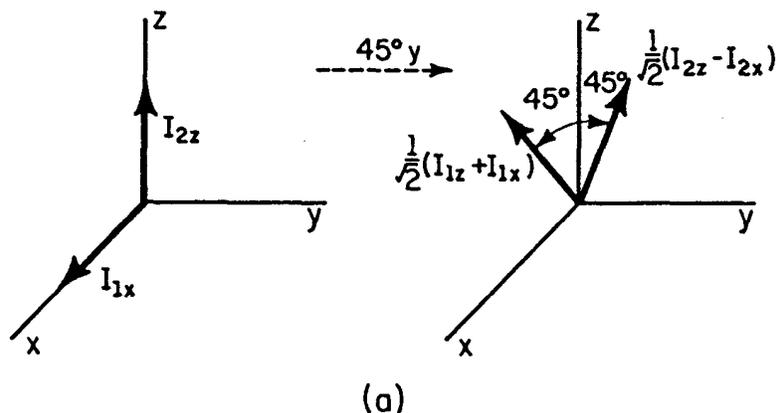
Up to now, we have not addressed the issue of how to distinguish the various n-quantum coherences. In eqn. 30 we have included only those terms in the density matrix which have come from 2-quantum coherence. Actually the signal should have contributions from 1-quantum as well as 2-quantum coherence. In general for N spin-1/2 nuclei, the signal should have contributions from all orders of coherence up to N-quantum coherence. One easy way to separate these various order of coherence is to tune the r.f. off resonance by  $\Delta\omega$ , and let the various order of coherence evolve for a time t' before converting them to 1-quantum coherence for observation (Figure 1b). In the appendix we include the off-resonance in the Hamiltonian, and treat the pulse sequence in detail.

One finds that the contribution from n-quantum coherence will have a t'-dependence of  $\cos(n\delta\omega t')$ . Therefore one can fix t' and observe the simulated-echo amplitude after the third pulse as a function of the time t'. If one then Fourier transforms the signal versus t', the n-quantum coherence will be centered at  $n\delta\omega$ .

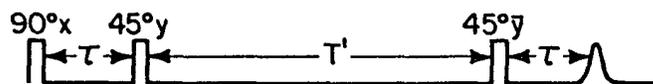
#### IV. DIPOLAR ORDER

Zeeman energy (or the degree of Zeeman order) is determined by the alignment of spins along the external magnetic field. Dipolar energy (or the degree of dipolar order), on the other hand, is determined by the alignment of spins in the local field produced by their neighbors. For two spin-1/2 nuclei with the dipolar coupling,  $\hbar a I_{1z}I_{2z}$ , the Zeeman energy can be described by  $\langle H_z \rangle = -\gamma \hbar H_0 \langle I_z \rangle$ , and the dipolar energy by  $\langle H_d \rangle = + \hbar a \langle I_{1z}I_{2z} \rangle$ . Hence  $\langle I_z \rangle$  gives the Zeeman order and  $\langle I_{1z}I_{2z} \rangle$  the dipolar order. From eqn. 8 the system at thermal equilibrium has largely Zeeman order.

The Zeeman order can be transferred to dipolar order by the well known method of adiabatic demagnetization in the rotating frame (13). In



(a)



(b)

MP-834

Figure 2. a)  $I_{1x}I_{2z}$  is rotated by a  $45^\circ_y$  pulse to give among other terms  $I_{1z}I_{2z}$ , which represents dipolar order. b) The pulse sequence for dipolar order experiments.

this method magnetization is first brought to align along the alternating field  $H_1$ . Then  $H_1$  is gradually reduced to zero in a time scale much longer than the spin-spin relaxation time  $T_2$ . An alternative, using two r.f. pulses ( $90^\circ_x$  and  $45^\circ_y$  separated by an interval of the order of  $T_2$ , to transfer the order was first proposed by Jeener and Broekaert (2). Thought not as efficient as adiabatic demagnetization, the pulse technique is convenient and can transfer the order in a rather short time, of the order of  $T_2$ .

Let us now analyze the Jeener-Broekaert sequence using the operator formalism. Again, starting with magnetization along the z-direction one applies a  $90^\circ_x$  pulse. From eqn. 21 the density matrix at a time  $\tau$  after the pulse contains a term

proportional to  $I_{1x}I_{2z} + I_{2x}I_{1z}$ . The Jeener-Broekaert trick is to transform this term to dipolar order ( $I_{1z}I_{2z}$ ) by a rotation. Since the angle between the two spins is invariant under a rotation, no rotation can perfectly transform  $I_{1x}I_{2z}$  (with a  $90^\circ$  angle between the two spins) to  $I_{1z}I_{2z}$  (with an angle of  $0^\circ$  between the two spins). The best one can do is to rotate the spins such that each spin is  $45^\circ$  off the z-axis. A  $45^\circ_y$  pulse accomplishes just that, as shown in Figure 2a. The density matrix after the  $45^\circ_y$  pulse is

$$\rho(\tau^+) = I_y \cos(a\tau/2) - [(I_{1x} + I_{1z})(I_{2z} - I_{2x}) + (I_{2x} + I_{2z})(I_{1z} - I_{1x})] \sin(a\tau/2) \quad (32)$$

The term proportional to  $I_{1z}I_{2z}$ , which corresponds to the dipolar order, will decay in a time scale of the spin-lattice relaxation time  $T_1$ , while the other terms will decay in a time scale of  $T_2$ . Since in most solids  $T_1$  is much longer than  $T_2$  after a time  $T'$  of several  $T_2$ , only the dipolar order remains:

$$\rho(\tau + T') = -2I_{1z}I_{2z}\sin(a\tau/2) \quad (33)$$

independent of  $T'$ . Note that the transfer of the Zeeman order to the dipolar order is maximized if  $\tau$  equals  $\pi/a$ .

Like multiquantum coherence the dipolar order is not directly observable as transverse magnetization since the term of  $I_{1z}I_{2z}$  contributes zero to  $\text{Tr}(I_x\rho)$  or  $\text{Tr}(I_y\rho)$ . To detect the dipolar order one can reverse the process and transfer the order back to Zeeman order (i.e. the magnetization along the z axis), either by adiabatic magnetization or by the pulse method. For the pulse method one can use the inverse of the previous sequence (i.e. we use  $45^\circ_{-y} - \tau - 90^\circ_{-x}$ ). One can then inspect the z-magnetization by later applying another  $90^\circ_x$  pulse to observe an FID. If one applies it immediately after the  $90^\circ_{-x}$ , the two cancel, which shows that if all we do is simply apply a  $45^\circ_{-y}$  pulse we will get an echo at  $\tau$  as shown in Figure 2b. Explicitly we see that the density matrix eqn. 33 immediately after the  $45^\circ_{-y}$  pulse becomes

$$\rho(\tau + T^+) = -(I_{1z}I_{2z} + I_{1x}I_{2z} + I_{1z}I_{2x} + I_{1x}I_{2x}) \sin(a\tau/2) \quad (34)$$

Note that  $I_{1x}I_{2z} + I_{2x}I_{1z}$  is just what we started with in eqn. 21. Evolution of eqn. 34 can be evaluated using eqn. 24 and eqn. 25. The result is

$$\rho(\tau + T' + \tau) = -(1/2)I_y \sin^2(a\tau/2) + \text{other terms giving no transverse magnetization} \quad (35)$$

The signal therefore starts from zero and reaches its maximum when  $\tau$  reaches  $\pi/a$ . The optimal

signal is 1/4 of that of a free induction decay, and also 1/4 of that in a perfect adiabatic demagnetization experiment. Since there are two transfers involved in the pulse sequence (one from Zeeman to dipolar, and the other from dipolar to Zeeman order) the maximum efficiency of a single transfer between the dipolar and Zeeman order by pulses is half of that of adiabatic demagnetization (2).

## V. SOLID ECHOES

Powles and Mansfield (14) first used a  $90^\circ_x - \tau - 90^\circ_y$  pulse sequence to observe so-called solid echoes for pairs of  $^1\text{H}$  spins. The solid echo is formed by refocusing the dipolar coupling, as the standard echo is formed by refocusing the field inhomogeneity. In contrast to the standard echo, which produces refocusing without loss of signal, the dipolar echo is in general smaller than the free induction signal. The technique is useful in eliminating amplifier recovery problems when measuring the  $^1\text{H}$  signal. The  $90^\circ_x - \tau - 90^\circ_y$  pulse sequence has also been used to refocus the quadrupole interaction for spin-1 nuclei, such as deuterium (15).

As usual one starts with a  $90^\circ_x$  pulse. The density matrix at a time  $\tau$  after the pulse is that in eqn. 21. To refocus the dipolar coupling one wants to apply a rotation  $\mathbf{R}$  such that the net effect is equivalent to that of reversing the sign of the spin-spin coupling. That is, one asks can one find an operator  $\mathbf{R}$  such that

$$\rho(\tau^+) = \mathbf{R}^{-1} [\exp(-iaI_{1z}I_{2z}\tau) \rho(0) \exp(iaI_{1z}I_{2z}\tau)] \mathbf{R} = \exp(iaI_{1z}I_{2z}\tau) \rho(0) \exp(-iaI_{1z}I_{2z}\tau) \quad (36)$$

If one can find such an  $\mathbf{R}$ , the dipolar coupling will be refocused at a time  $\tau$  after the second pulse, (which produces  $\mathbf{R}$ ) so that:

$$\rho(2\tau) = \rho(0) \quad (37)$$

Eqn. 36 tells us that the effect of  $\mathbf{R}$  is to replace a by -a. Thus, using eqn. 21 for  $\rho(\tau^-)$  we want

$$\rho(\tau^+) =$$

$$I_y \cos(a\tau/2) + 2(I_{1x}I_{2z} + I_{2x}I_{1z})\sin(a\tau/2) \quad (38)$$

Comparing eqn. 21 and eqn. 38 one finds that one wants to keep  $I_y$  invariant, but reverse the sign of  $I_{1x}I_{2z} + I_{2x}I_{1z}$ . This can be accomplished by a  $90^\circ_y$  pulse.

Although the refocusing is perfect for an isolated pair of nuclei, for systems involving more spins the system does not refocus perfectly. It can be shown that, for three spin-1/2 nuclei equally coupled to one another, the amplitude of the echo is reduced by a factor of 4. For pairs of spins the coupling between pairs also causes a decay of the signal as the pulse separation  $\tau$  is increased.

## VI. HETERONUCLEAR COHERENCE TRANSFER

In 1956 George Feher (16) discovered a double resonance method for transferring electron polarization to nuclei. He was studying the  $^{31}\text{P}$  donor centers in silicon. His method consisted of two successive adiabatic sweeps. The first frequency sweep went across one of the two electron hyperfine lines inverting the corresponding populations. It was followed by the sweep of a second oscillator across one of the two nuclear hyperfine lines performing a second population inversion. The resulting population has transferred the metal electron polarization to the nuclei. This method differs from the Overhauser effect in that the transfer of coherence from the electron to the nucleus does not result from relaxation phenomena. The same effect can be achieved by a pulsed double resonance method. One first applies a  $90^\circ_x$  pulse, followed at the proper time by a  $90^\circ_y$  pulse to the electrons. This is equivalent to an adiabatic passage across one electron hyperfine line. One then does the same to the nuclei. Such a pulsed approach was first proposed by Maudsley and Ernst (17) who apply 3 instead of 4  $90^\circ$  pulses. By omitting the final  $90^\circ$  pulse, they obtained magnetization which was transverse rather than longitudinal. The pulsed method can be used in a modified 2D spectroscopy

technique to obtain detailed information on the structure of the spin system and the connectivity of transitions directly.

Maudsley and Ernst (17) first proposed their method to record indirectly with enhanced sensitivity the NMR of nuclei with a low gyromagnetic ratio (S spin) by a coherent transfer of transverse magnetization to nuclei of high gyromagnetic ratio (I spin). The S spin coherence is first created by a  $90^\circ_x$  pulse. After a certain time  $\tau_1$  two  $90^\circ_y$  pulses (one for the S spin, and the other for the I spin) are applied simultaneously to transfer the transverse magnetization from the S spin to the I spin.

Let us again examine two coupled spin-1/2 nuclei with the coupling

$$H_C = \hbar a I_z S_z \quad (39)$$

Assume that initially there is only S spin magnetization, so that no I spin magnetization can be observed without a transfer of magnetization. The first  $90^\circ_x$  pulse for the S spin creates S spin coherence,

$$\rho(\sigma^+) = S_y \quad (40)$$

At a time  $t_1$  after the pulse the density matrix is similar to that of eqn. 21.

$$\rho(t_1) = S_y \cos(at_1/2) - 2S_x I_z \sin(at_1/2) \quad (41)$$

One can see that the hope of transferring coherence to the I spin lies with the term of  $S_x I_z$ . Note also that if one has started with I spin echoes the density matrix would have contained a term of  $I_x S_z$ . So to have a heteronuclear coherence transfer, one only needs to transform  $S_x I_z$  to  $I_x S_z$ . To transform  $S_x$  to  $S_z$ , we need a  $90^\circ_y$  pulse for the S spin. To transform  $I_z$  to  $I_x$ , we need another  $90^\circ_y$  pulse for the I spin. We therefore need two  $90^\circ_y$  pulses for the S spin and the I spin respectively as shown in Figure 3.

The density matrix after the two  $90^\circ_y$  pulses is

$$\rho(t_1^+) = S_y \cos(at_1/2) + 2 I_x S_z \sin(at_1/2) \quad (42)$$

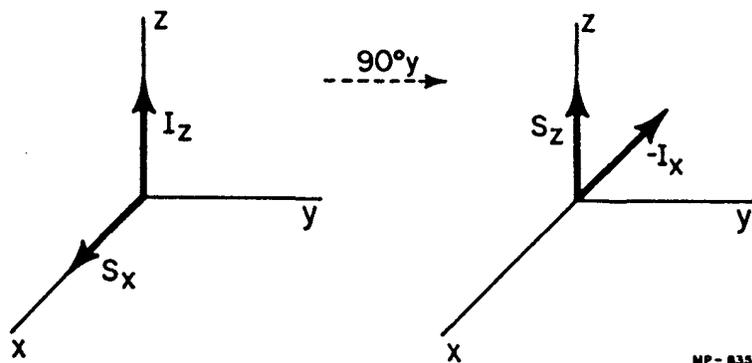


Figure 3. The S spin coherence.  $S_x I_z$ , is rotated by two  $90^\circ_y$  pulses (one for the S spin and the other for the I spin) to give I spin coherence,  $-S_z I_x$ .

Since we are only concerned with I spin magnetization, we keep only the second term. Using eqn. 24 the evolution of  $\rho$  is obtained as

$$\rho(t_1 + t_2) = 2 I_x S_z \sin(at_1/2) \cos(at_2/2) + I_y \sin(at_1/2) \sin(at_2/2) \quad (43)$$

S spin transverse magnetization has therefore been transferred to I spin transverse magnetization, which, with a larger  $\gamma$ , gives an enhanced signal. This effect can be utilized in a two dimensional spectroscopy technique to obtain detailed information of the structure of the spin system and the connectivity of the transitions (16).

## VII. SUMMARY

In summary we have given a quantum mechanical treatment of two spin-1/2 nuclei coupled via  $\hbar a I_{1z} I_{2z}$ . We have used the density matrix to describe the state of the system. We have expressed the density matrix as a linear

combination of  $I$ ,  $I_{1\alpha}$ ,  $I_{2\beta}$ , and  $I_{1\alpha} I_{2\beta}$ . The effect of rf pulses is simply that of classical rotations. The effect of spin-spin coupling on the evolution of spins is also somewhat similar to that of classical pictures (see eqn. 20). The description of various pulse sequences thus becomes straightforward, and one can actually "see" how different pulse sequences work and how they are related to one another. The simplicity and pictorial nature of this method should prove itself a useful tool in designing pulse sequences.

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## APPENDIX

In this appendix we describe the complete multiquantum coherence experiment (Fig. 1b) for two spin-1/2 nuclei, with spin-spin coupling and an off-resonance effect:

$$H_C = \hbar a I_{1z} I_{2z} + \hbar \delta \omega I_z \quad (44)$$

Let us denote the evolution under spin-spin coupling,  $\exp(i a I_{1z} I_{2z} t)$ , by  $T$ , then the evolution after the first  $90^\circ_x$  pulse is

$$\begin{aligned} \rho(t) &= \exp(-i H_C t / \hbar) \rho(0) \exp(i H_C t / \hbar) = \\ &\exp(-i \delta \omega I_z t) [T^{-1} (I_{1y} + I_{2y}) T] \exp(i \delta \omega I_z t) \end{aligned} \quad (45)$$

The evolution of  $I_{1y}$  and  $I_{2y}$  under spin-spin coupling has been described in eqn. 24. The effect of the off-resonance is simply precession about the z-axis. From eqn. 15 and eqn. 24 we obtain

$$\begin{aligned} \rho(t) &= \exp(-i \delta \omega I_z t) [I_y \cos(at/2) - \\ &2(I_{1x} I_{2z} + I_{2x} I_{1z}) \sin(at/2)] \exp(i \delta \omega I_z t) \\ &= [I_y \cos(\delta \omega t) - I_x \sin(\delta \omega t)] \cos(at/2) - \\ &- 2(I_{1x} I_{2z} + I_{2x} I_{1z}) \cos(\delta \omega t) \sin(at/2) \\ &- 2(I_{1y} I_{2z} + I_{2y} I_{1z}) \sin(\delta \omega t) \sin(at/2) \end{aligned} \quad (46)$$

After the second  $90^\circ_x$  pulse, the density matrix is

$$\begin{aligned} \rho(t^+) &= -I_z \cos(\delta \omega t) \cos(at/2) \\ &- [I_x \sin(\delta \omega t)] \cos(at/2) \\ &- 2(I_{1z} I_{2y} + I_{2z} I_{1y}) \sin(\delta \omega t) \sin(at/2) \\ &- 2(I_{1x} I_{2y} + I_{2x} I_{1y}) \cos(\delta \omega t) \sin(at/2). \end{aligned} \quad (47)$$

The first term contains 0-quantum, the second term 1-quantum, and the third term 2-quantum coherence. Let us now follow the three terms separately.

Let us first consider the evolution of the 2-quantum coherence. Let us consider the effect of spin-spin coupling and of being off-resonance on the evolution of 2-quantum coherence separately. The spin-spin coupling has no effect on the evolution of 2-quantum coherence. In other words the frequency of the two quantum coherence is the same as though the spins did not interact. This is because the spin-spin coupling shifts the energy of the state with both spins pointing up and that of the state with both spins pointing down by the same amount. Hence the energy splitting between the two states is not affected by the coupling.

Mathematically this can be seen from the evolution of the  $\Delta m = 2$  density matrix element:

$$\langle \frac{1}{2}, \frac{1}{2} | \exp(-i a I_{1z} I_{2z} t) I_1^+ I_2^+ \exp(i a I_{1z} I_{2z} t) | -\frac{1}{2}, -\frac{1}{2} \rangle \quad (48a)$$

which, allowing the right hand exponential to operate to the right, the left hand one to operate to the left, gives

$$\begin{aligned} &\langle \frac{1}{2}, \frac{1}{2} | \exp(-i a t / 4) I_1^+ I_2^+ \exp(i a t / 4) | -\frac{1}{2}, -\frac{1}{2} \rangle \\ &= \langle \frac{1}{2}, \frac{1}{2} | I_1^+ I_2^+ | -\frac{1}{2}, -\frac{1}{2} \rangle \\ &= 1. \end{aligned} \quad (48b)$$

The  $\Delta m = 2$  matrix element therefore stays as a constant with time under the spin-spin coupling. Alternatively we can follow our regular approach, and calculate the evolution of the 2-quantum term ( $I_{1x} I_{2y} + I_{2x} I_{1y}$ ) under the spin-spin coupling

$$\begin{aligned} &T^{-1} (I_{1x} I_{2y} + I_{2x} I_{1y}) T \\ &= (T^{-1} I_{1x} T) (T^{-1} I_{2y} T) + (T^{-1} I_{2x} T) (T^{-1} I_{1y} T). \end{aligned} \quad (49)$$

This can be easily evaluated using eqn. 24 to obtain

$$\begin{aligned} &T^{-1} (I_{1x} I_{2y} + I_{2x} I_{1y}) T \\ &= I_{1x} I_{2y} \cos^2(at/2) - 4 I_{1y} I_{2z} I_{2x} I_{1z} \sin^2(at/2) \\ &+ I_{2x} I_{1y} \cos^2(at/2) - 4 I_{2y} I_{1z} I_{1x} I_{2z} \sin^2(at/2) \end{aligned}$$

$$= I_{1x}I_{2y} + I_{2x}I_{1y} \quad (50)$$

In arriving at the final result, we have used the cyclic property of Pauli's matrices that  $\sigma_x\sigma_y = i\sigma_z$ , and so on. Eqn. 50 again shows that spin-spin coupling has no effect on the evolution of 2-quantum coherence for two spin-1/2 nuclei. In general spin-spin coupling has no effect on the evolution of N-quantum coherence for N spin-1/2 nuclei.

The effect of off-resonance on the other hand is amplified for 2-quantum coherence. If we denote the precession about the z-axis due to off-resonance,  $\exp(i\delta\omega I_z t)$ , by P, we have

$$P^{-1}(I_{1x}I_{2y} + I_{1y}I_{2x})P = \\ (P^{-1}I_{1x}P)(P^{-1}I_{2y}P) + (P^{-1}I_{1y}P)(P^{-1}I_{2x}P) \quad (51)$$

Using eqn. 15 to evaluate the precession of spins, we obtain

$$[P^{-1}(I_{1x}I_{2y} + I_{1y}I_{2x})P] \\ = (I_{1x}I_{2y} + I_{1y}I_{2x})\cos(2\delta\omega t) + \\ (I_{1y}I_{2y} - I_{1x}I_{2x})\sin(2\delta\omega t). \quad (52)$$

Therefore 2-quantum coherence precesses at twice the off-resonance frequency. This can also be proved by first using eqn. 15 to show that

$$P^{-1}I_i^+P = I_i^+ \exp(-i\delta\omega t) \quad (53)$$

It then follows that for n-quantum coherence

$$P^{-1}(I_1^+ I_2^+ \dots I_n^+)P = \\ (P^{-1}I_1^+P) \dots (P^{-1}I_n^+P) \\ = (I_1^+ I_2^+ \dots I_n^+) \exp(-in\delta\omega t) \quad (54)$$

Combining eqn. 47, eqn. 50 and eqn. 52, we have the evolution of the 2-quantum term in the density matrix as

$$\rho_{2q}(t+t') = \\ (P^{-1}T^{-1}(I_{1x}I_{2y} + I_{2x}I_{1y})TP)[-2\cos(\delta\omega t) \sin(at/2)] \\ = [(I_{1x}I_{2y} + I_{2x}I_{1y})\cos(2\delta\omega t) + \\ (I_{1y}I_{2y} - I_{1x}I_{2x})\sin(2\delta\omega t)] [-2\cos(\delta\omega t)\sin(at/2)] \quad (55)$$

This is converted back to 1-quantum coherence by the third  $90^\circ_{-x}$  pulse for inspection:

$$\rho_{2q}(t+t'^+) = \\ -2(I_{1x}I_{2z} + I_{2x}I_{1z})\cos(\delta\omega t)\sin(at/2) \cos(2\delta\omega t) \\ + 0\text{-quantum and 2-quantum terms} \quad (56)$$

We can omit the 0-quantum and 2-quantum terms, since they do not contribute to transverse magnetization. After another evolution period of t, a stimulated echo appears. To calculate the evolution of  $I_{1x}I_{2z}$  and  $I_{2x}I_{1z}$ , we note that  $I_{1z}$  and  $I_{2z}$  commute with T and P and do not evolve with time. The evolution  $I_{1x}$  and  $I_{2x}$  is similar to that of  $I_{1y}$  and  $I_{2y}$ , which has been obtained in eqn. 46. The result can therefore be easily obtained as

$$\rho_{2q}(t+t'+t) = \\ -4(I_{1y}I_{2z}^2 + I_{2y}I_{1z}^2)\cos^2(\delta\omega t)\sin^2(at/2)\cos(2\delta\omega t) \\ + 4(I_{1x}I_{2z}^2 + I_{2x}I_{1z}^2)\cos(\delta\omega t)\sin(\delta\omega t) \times \\ \sin^2(at/2)\cos(2\delta\omega t) \\ + \text{terms giving no transverse magnetization} \quad (57)$$

The contribution from 2-quantum coherence to the stimulated echo amplitude is therefore

$$\langle I_y \rangle_{2q} = -2\cos^2(\delta\omega t)\sin^2(at/2)\cos(2\delta\omega t) \\ \langle I_x \rangle_{2q} = 2\cos(\delta\omega t)\sin(\delta\omega t)\sin^2(at/2) \cos(2\delta\omega t) \quad (58)$$

Similarly we can calculate the evolution of  $\rho_{1q}(t^+)$ , the 1-quantum term in  $\rho(t^+)$ .  $\rho_{1q}(t^+)$  is the second term in eqn. 47. From eqn. 24, we obtain

$$T^{-1} \rho_{1q}(t^+) T = -I_x \cos(a(t'-t)/2) \sin(\delta\omega t) \\ - 2(I_{1z}I_{2y} + I_{2z}I_{1y}) \sin(a(t'-t)/2) \sin(\delta\omega t) \quad (59)$$

The effect of off-resonance is to cause  $I_x$ ,  $I_{1y}$ , and  $I_{2y}$  to precess about the z-axis with angular velocity  $\delta\omega$ . At the end of the evolution period  $t'$ , the  $90^\circ_{-x}$  pulse will give then

$$\rho_{1q}(t+t^+) = \\ -I_x \cos(\delta\omega t') \cos(a(t'-t)/2) \sin(\delta\omega t) \quad (60) \\ + 2(I_{1z}I_{2y} + I_{2z}I_{1y}) \cos(\delta\omega t') \sin(a(t'-t)/2) \sin(\delta\omega t) \\ + \text{terms giving no transverse magnetization.}$$

At the time of the stimulated echo, the contribution of 1-quantum coherence to the transverse magnetization can be obtained as

$$\langle I_y \rangle_{1q} = -2 \cos(a(t'-2t)/2) \sin^2(\delta\omega t) \cos(\delta\omega t') \\ \langle I_x \rangle_{1q} = -2 \cos(a(t'-2t)/2) \sin(\delta\omega t) \cos(\delta\omega t) \cos(\delta\omega t') \quad (61)$$

Lastly the evolution of  $\rho_{0q}(t^+)$ , the 0-quantum term in  $\rho(t^+)$ , is easily evaluated. The 0-quantum term,  $I_z$ , commutes with  $H_C$ , and therefore stays constant during the evolution period  $t'$ . The third  $90^\circ_{-x}$  pulse then transforms  $I_z$  to  $I_y$ , which contributes to the transverse magnetization at the time of the stimulated echo:

$$\langle I_y \rangle_{0q} = -2 \cos^2(\delta\omega t) \cos^2(at/2) \\ \langle I_x \rangle_{0q} = +2 \sin(\delta\omega t) \cos(\delta\omega t) \cos^2(at/2) \quad (62)$$

In the multiquantum coherence experiment (Figure 1b) we can fix the time  $t$ , and record the stimulated echo amplitude as a function of the evolution time  $t'$ . We then do a Fourier transform. From eqn. 58, eqn. 6, and eqn. 62, we find that the contributions from 0-quantum, 1-quantum and

2-quantum coherence at frequencies of 0,  $\delta\omega$ , and  $2\delta\omega$  respectively. They are therefore well separated. Both 0-quantum and 2-quantum lines are singlets, while the 1-quantum line is split by the spin-spin coupling into a doublet.

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