# Encoding multiple quantum coherences in non-commuting bases

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## Abstract

Multiple quantum (MQ) coherences are characterized by their coherence number and the number of spins that make up the state, though only the coherence number is normally measured. We present a simple set of measurements that extend our knowledge of the MQ state by recording the coherences in two non-commuting bases – the $x$ and the $z$ bases (related by a similarity transformation). The measurement of coherences in a basis other than the usual $z$ basis also permits the study of spin dynamics under Hamiltonians that conserve $z$ basis coherence number.
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## 1. Introduction

The many-body behavior of nuclear spins in a solid was described, for a long time, in the language of spin thermodynamics [1–3]. This description is, however, essentially static, and the dynamical behavior of the system was typically ignored, or addressed in terms of memory functions [4,5]. With the advent of multiple quantum NMR techniques [6–9], multi-spin processes could be described by multiple spin correlations and multiple quantum (MQ) coherences. The selective excitation and transformation [10] of MQ coherences led to a new picture of many-body spin dynamics in a dipolar solid [11–14]. The focus in these experiments was on transitions of coherence number, which were observable, rather than the number of spins involved in the MQ coherence states. However, the object of the experiment continued to be 'spin counting' as these MQ experiments were called. These techniques have been used to probe the spatial relationships between spins in large macromolecules, polymers and crystalline systems, including determining the dimensionality and size of localized spin clusters (see [15–18] for reviews).

In principle, all the spins in a solid are coupled together through their dipolar fields, and the Hilbert space of the spin system is determined by the total number of spins in the sample. However, at high field and for temperatures above a few degrees Kelvin, it is sufficient to consider a much smaller spin system to predict the NMR spectrum of a solid [19]. The sample resembles an ensemble of weakly coupled subsystems, within each of which an effective number of coupled spins is

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postulated to exist. In equilibrium, at high field, the spin number is one, as $\rho \approx \sum_i I_z^i$.

In a strong magnetic field ($B_0\hat{z}$), an $N$ spin-1/2 system has $2^N$ stationary states. These can be classified according to the magnetic quantum number, $M_z = \sum_i m_{zi} = (n_{|+1/2\rangle} - n_{|-1/2\rangle})/2$, where $m_{zi} = \pm 1/2$ is the eigenvalue of the $i$th spin in the system, and the energy eigenvalue corresponding to $M_z$ is $E_z = -\gamma\hbar B_0 M_z$. For non-degenerate stationary states there are on the order of $2^{2N-1}$ possible transitions between any two levels. The difference in $M_z$ values between the two levels is referred to as the *coherence number*.

While these coherences refer to transitions between levels, it is useful to discuss multiple quantum coherences for states of a system. When the state is expressed in the eigenbasis of the system, the presence of a non-zero matrix element $\langle z_i|\rho|z_j\rangle$, indicates the presence of an $n$ quantum coherence, where $n = M_z(z_j) - M_z(z_i)$. Since $M_z = \sum_i m_{zi}$ is a good quantum number, we use a collective rotation about the axis of quantization, $\sum_i I_z^i$, to characterize it

$$\langle z_i| \exp\left(-\mathrm{i}\phi \sum_i I_z^i\right)\rho \exp\left(+\mathrm{i}\phi \sum_i I_z^i\right)|z_j\rangle$$
$$= \exp(\mathrm{i}n\phi)\langle z_i|\rho|z_j\rangle. \tag{1}$$

If the density operator is expanded in the basis of irreducible tensor operators $T_{lm}$,

$$\rho = \sum_{lm} a_{lm} T_{lm} \tag{2}$$

the rank $l$ of the tensor element defines the spin number, while the order $m$ characterizes the coherence number.

In the usual MQNMR experiment, the system (initially in Zeeman equilibrium) is allowed to evolve under the action of a Hamiltonian that generates single quantum (SQ) [20], or double quantum (DQ) [10,21] transitions. This progressively increases the coherence numbers of the state of the system, as well as causing its spin number to increase.

While the coherences have a physical meaning in the eigenbasis of the system, a generalized coherence number reports on the response of the system to any collective rotation of the spins

(about the $x$ axis for example). This is equivalent to expressing the state of the spins in a basis where the apparent axis of quantization is given by the axis of rotation, and can be obtained from the eigenbasis via a similarity transformation. For example, the similarity transform $\mathscr{P}$ connects the density matrices of the system in the two (the $z$ or eigen-basis, and the $x$ basis) representations.

$$[\rho^x] = \mathscr{P}^{-1}[\rho^z]\mathscr{P}, \tag{3}$$

where the elements of the matrices are $[\rho^x]_{ij} = \langle x_i|\rho|x_j\rangle$, $[\rho^z]_{ij} = \langle z_i|\rho|z_j\rangle$ and $\{x_i\}$ and $\{z_i\}$ are complete sets of basis operators. Under a collective rotation about the $x$ axis, we obtain,

$$\langle x_i| \exp\left(-\mathrm{i}\phi \sum_i I_x^i\right)\rho \exp\left(+\mathrm{i}\phi \sum_i I_x^i\right)|x_j\rangle$$
$$= \exp(\mathrm{i}n\phi)\langle x_i|\rho|x_j\rangle, \tag{4}$$

where $n$ is the $x$ basis coherence number. Similarity transformations do not change the eigen-energies or the physics of the system [22]. Suter and Pearson [23] previously used a combination of phase shifts and a variable flip angle pulse to encode for coherences in the $y$ basis as well as the $z$ basis. Their technique was recently used to study the dynamics of polarization and coherence echoes [24]. Requantization in an alternative basis has also been applied to analyzing RF gradient NMR spectroscopy [25].

In this Letter we demonstrate an improved technique for the encoding of coherences in the $x$ basis as well as for encoding coherences simultaneously in the $x$ and $z$ bases. While the measurement of coherence number in an orthogonal basis does provide more information about the state, it does not yield a direct measure of the spin number. Under a collective rotation of the spins, the different orders within a given rank are mixed, but there is no mixing between terms of different rank. Thus, contributions to a given coherence order from the different ranked tensors cannot be separated out, without some measure of the distribution of tensor ranks in the system. In order to unambiguosly determine the spin number, $N$-independent measurements are required.

Measurements in non-commuting basis are central to the task of quantum state tomography.

Eigenbasis measurements provide information on the amplitudes of the terms in the density matrix (in the eigenbasis), but not on the associated phase factors. Changing the basis and repeating the measurements allows reconstruction of the exact state of the system, a familiar process used to measure the Wigner function in optics experiments [26]. Measuring multiple quantum coherences in a basis other than the usual $z$ basis is particularly important if we wish to study the dynamics of the spin system under a Hamiltonian that conserves $z$ basis coherence number, such as the secular dipolar Hamiltonian.

## 2. Methods

Table 1 shows the initial state, Hamiltonian, and selection rules for the standard MQ experiment (using a DQ Hamiltonian), in both the standard $z$ basis and the $x$ basis. Reference [25] tabulates the transformations between quantization in the different Cartesian bases. Thus, starting from an initial Zeeman state, we see that under the DQ Hamiltonian we should get only even order coherences in the $z$ basis and only odd order coherences in the $x$ basis.

The experimental methods presented here improve on those of Suter and Pearson, as their variable flip angle pulse is replaced by a sequence of phase shifted pulses, whose duration is fixed. The dipolar evolution during the variable angle pulse, as it is sampled out to multiples of $2\pi$, can signifi-

cantly attenuate the signal and compromise the resolution of the coherences in the $x$ or $y$ basis, especially in a strongly dipolar coupled system. In our experiment, the dipolar evolution is refocused, and the $\phi I_x$ rotation achieved purely with phase shifts.

The pulse sequences shown in Fig. 1a,b allow us to encode coherences in the two bases under essentially identical conditions. Fig. 1a is a $z$ basis encoding experiment while Fig. 1b is an $x$ basis encoding experiment. The only difference between the two is that the first $\pi/2$ pulse is phase shifted along with $U_\phi$ in the $x$ basis experiment. Fig. 1c shows the 16 pulse DQ selective sequence used. It consists of two cycles of the standard 8 pulse sequence, phase shifted by $\pi$ with respect to each other. The sequence compensates for pulse imperfections and resonance offsets. $U_\phi$ is created by phase shifting all the pulses in the 16 pulse experiment by $\phi$. The two ($\pi/2$) pulses and the Cory 48-pulse sequence are not required for the $z$ basis experiment. However, they are included in order to perform the two experiments under identical conditions. In the $x$ basis experiment, the two ($\pi/2$) pulses perform the basis transformation, and the phase encoding of the coherences. Placing them back-to-back leads to unwanted switching transients, so they are separated by the Cory 48-pulse sequence which prevents evolution of the spin system under the secular dipolar Hamiltonian between the two ($\pi/2$) pulses, and has been described previously [27].

The operator corresponding to the observable signal is $I_z$. The measured signal for the experiment

Table 1
Description of the MQ experiment in the $z$ and $x$ bases

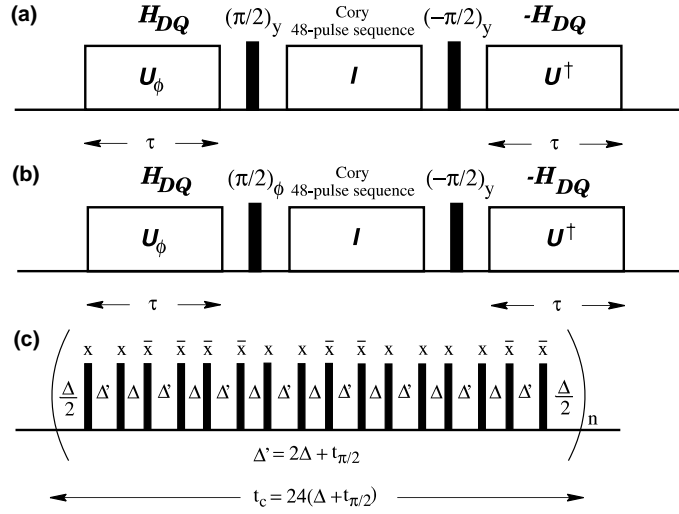| | $z$ basis | $x$ basis |
|---|---|---|
| Initial state | $I_z$ | $-\dfrac{\iota}{2}\left\{I_x^+ - I_x^-\right\}$ |
| Initial coherence number | 0 | $\pm 1$ |
| MQ Hamiltonian | $\sum_{i<j} d_{ij}\left\{I_i^+ I_j^+ + I_i^- I_j^-\right\}$ | $\sum_{i<j} d_{ij}\left[\left\{2I_{xi}I_{xj} - \dfrac{1}{2}\left(I_{xi}^+ I_{xj}^- + I_{xi}^- I_{xj}^+\right)\right\} - \dfrac{1}{2}\left\{I_{xi}^+ I_{xj}^+ + I_{xi}^- I_{xj}^-\right\}\right]$ |
| Coherence number selection rule | $\pm 2$ | $0, \pm 2$ |
| Spin number selection rule | $\pm 1$ | $\pm 1$ |
| Coherences | Even | Odd |

Fig. 1. (a) The $z$ basis encoding experiment, $U_\phi = R_z(-\phi)UR_z(\phi)$, and $U = \exp(iH_{DQ}\tau)$. The propagator for the 48 pulse time-suspension sequence is the Identity Operator I. (b) The $x$ basis encoding experiment, where the first $(\pi/2)$ pulse is phase shifted, $(\pi/2)_\phi = R_z(-\phi)(\pi/2)_y R_z(\phi)$. (c) The 16 pulse sequence used to generate the effective DQ Hamiltonian; $\Delta = 1.3$ μs, $t_{\pi/2} = 0.51$ μs, $t_c = 43.4$ μs.

in Fig. 1a corresponds to $\langle I_z \rangle_\phi = Tr[\rho_f I_z]$, where the final density matrix is given by

$$\rho_f = U^\dagger R_y(-\pi/2)R_y(\pi/2)U_\phi \rho_i U_\phi^\dagger R_y(-\pi/2)R_y(\pi/2)U$$
$$= U^\dagger R_z(-\phi)UI_z U^\dagger R_z(\phi)U, \tag{5}$$

where $R_\alpha(\phi) = \exp(i\phi I_\alpha)$, and we have used the fact that the initial state $I_z$ is invariant to $z$-rotations. Defining $\rho_s = U\rho_i U^\dagger = UI_z U^\dagger$, the state of the system after evolution under the DQ Hamiltonian, we obtain the measured signal in the $z$ basis experiment

$$\langle I_z \rangle_\phi = Tr[R_z(-\phi)\rho_s R_z(\phi)\rho_s]. \tag{6}$$

For the experiment in Fig. 1b, the final density matrix is given by

$$\rho_f = U^\dagger R_y(-\pi/2)R_\phi(\pi/2)U_\phi \rho_i U_\phi^\dagger R_\phi$$
$$\quad \times (-\pi/2)R_y(\pi/2)U$$
$$= U^\dagger R_y(-\pi/2)R_z(-\phi)R_y(\pi/2)UI_z U^\dagger R_y$$
$$\quad \times (-\pi/2)R_z(\phi)R_y(\pi/2)U$$
$$= U^\dagger R_x(-\phi)UI_z U^\dagger R_x(\phi)U \tag{7}$$

and the observed magnetization in the $x$ basis experiment is

$$\langle I_z \rangle_\phi = Tr[R_x(-\phi)\rho_s R_x(\phi)\rho_s]. \tag{8}$$

In both cases, the experiment is repeated multiple times as $\phi$ is uniformly sampled out to a multiple of $2\pi$, and the resulting data Fourier transformed with respect to $\phi$ to obtain the distribution of coherence numbers.

Note that if Eqs. (6) and (8) could be written in terms of $\langle I_z \rangle_\phi = Tr[A(\phi)\rho_s]$, where the set of operators $A(\phi)$ form a complete basis for the Hilbert space of the spin system, it would be possible to perform quantum state tomography on the spins [26]. However, the experiments described here cannot completely characterize the state, or even just its collective properties.

## 3. Results

The experiments were performed at 2.35 T with a Bruker Avance spectrometer and a home-built RF probe. The 90° pulse time was 0.51 μs. The pulse spacing $\Delta$ used in the DQ sequence was 1.3 μs, and the cycle time for the 16 pulse cycle was 43.4 μs. The pulse spacing in the Cory 48-pulse sequence was 1.5 μs. The $T_1$ of the single crystal calcium fluoride sample used was

7 s, and the recycle delay used in the experiment was 10 s.

Fig. 2 shows the results obtained in the $z$ and $x$ basis encoding experiments. The maximum coherence encoded was $\pm 32$, with $\Delta\phi = 2\pi/64$. The phase incrementation was carried out to $8\pi$. It is seen that the $z$ and $x$ basis measurements give only even and odd coherences, respectively, as expected from Table 1. The data shown correspond to 1, 3 and 5 loops of the 16 pulse cycle. The higher order coherences are seen to grow in both bases, as the system evolves under the DQ Hamiltonian.

In Fig. 3 we plot the effective spin number, obtained by a Gaussian fit to the coherence number distributions in the $x$ and $z$ bases ($N(\tau) = 2\sigma^2$) as a function of $\tau$ [11]. The fits were performed on the 1D data. The variance of the $x$ basis measurements is consistently smaller than that of the $z$ basis measurements. The points appear to lie on a straight line, and a best linear fit has a slope of 0.54, which is very close to the value of 0.5 expected from the ratio between the double quantum selective terms in the DQ Hamiltonian
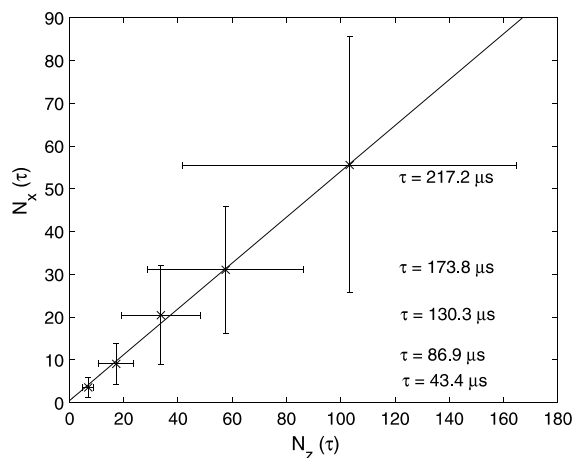


Fig. 3. Plot of the effective spin number ($N(\tau) = 2\sigma^2$) obtained by fitting the coherence distributions obtained in the 1D $x$ and $z$ basis measurements to a Gaussian. Also shown is the best linear fit to the data, whose slope is 0.54. The slope expected from the coefficient of the DQ selective terms in the two bases (see Table 1) is 0.5.

expressed in the two bases, as shown in Table 1. The linear fit was performed on the mean spin numbers $N_x$ and $N_z$ without considering the stan-
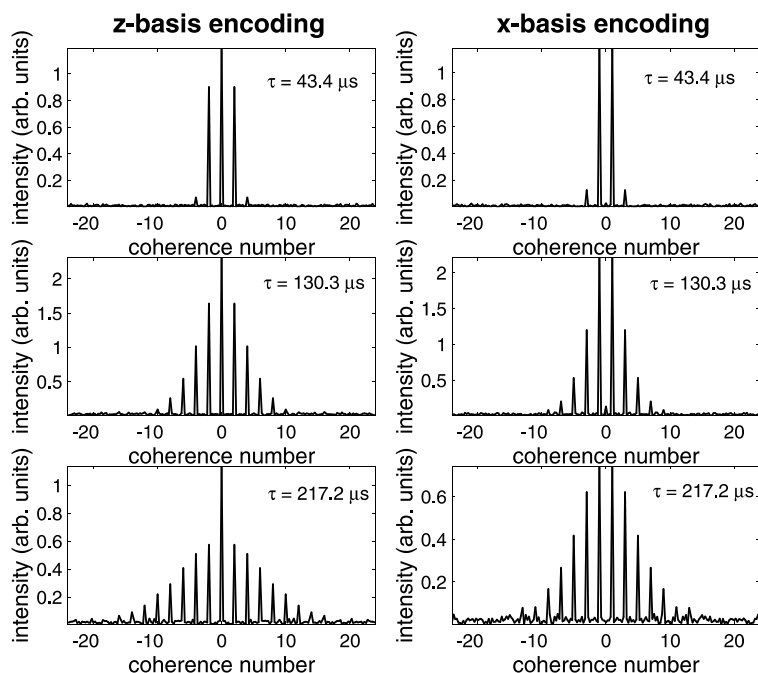


Fig. 2. Comparison of $z$ basis and $x$ basis coherences at preparations times $\tau = 43.4$, 130.3 and 217.2 μs, corresponding to 1, 3 and 5 loops of the 16 pulse cycle in Fig. 1c, showing the presence of purely even and odd coherences in the two bases, respectively.

dard deviations. The error in the fit is negligible. In the $z$ basis, evolution under the DQ Hamiltonian forces the system to change coherence number, while in the $x$ basis the presence of zero quantum terms permits mixing without changing the coherence number. Thus, the growth of the coherence numbers is slowed relative to the $z$ basis, leading to a narrower distribution. It should be emphasised that the basis change does not change the spin number, only the experimentally observable coherences. The change in spin number with basis representation demonstrates the limitations of the Gaussian statistical model as an accurate predictor of spin number in strongly coupled spin systems. Lacelle has also discussed the limitations of the model [17].

As first shown by Suter and Pearson [23], a 2D experiment illustrates the correlation between $x$ and $z$ basis coherences. The 2D experiment is obtained from the $x$ basis experiment in Fig. 1b by phase cycling the refocussing sequence $U^{\dagger}$ by $\beta$ independently of $\phi$. The phases $\phi$ and $\beta$ are incremented independently to sample a rectangular grid and a 2D Fourier transform is performed to yield the coherences. The measured data in a single experiment is

$$\langle I_z \rangle_{\beta\phi} = Tr[R_z(-\beta)R_x(-\phi)\rho_s R_x(\phi)R_z(\beta)\rho_s]. \quad (9)$$

It is straightforward to show that the order of the $x$ and $z$ phase shifts does not matter when both of them are sampled over a $2\pi$ range. The $(\phi_x)(\beta_z)$ experiment is equivalent to the $(-\beta_z)(-\phi_x)$ experiment. The 2D experiment separates out the different terms that contribute to a particular $z$ basis coherence as can be seen in Fig. 4. We used $\tau = 130.3$ μs, corresponding to 3 loops of the MQ cycle. The maximum coherence encoded in each direction was $\pm 12$, with $\Delta\phi = 2\pi/24$. The phase incrementation was carried out to $8\pi$ along each axis, resulting in a $96 \times 96$ data grid, which was Fourier transformed to yield the coherences shown.

This 2D technique can be used to examine the evolution of multiple quantum coherences under the dipolar Hamiltonian. Fig. 5 shows the attenuation of the $z$ basis zero quantum signal as it evolves under the dipolar Hamiltonian. Also
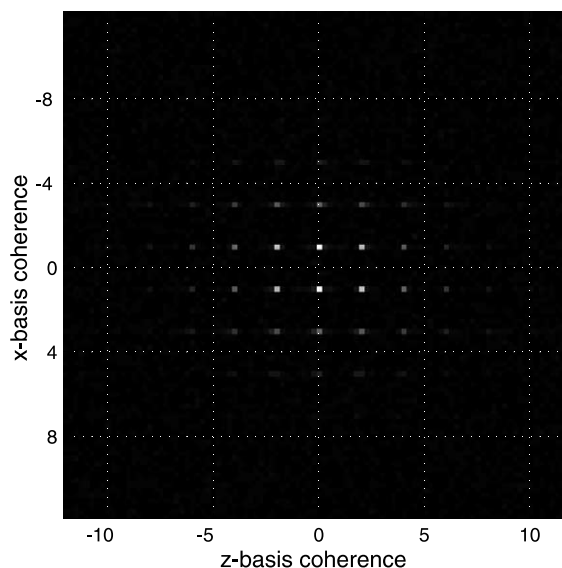


Fig. 4. Results of the 2D experiment – showing correlations between encoding in the $x$ and $z$ bases. The preparation time used was $\tau = 130.3$ μs, corresponding to 3 loops of the 16 pulse cycle in Fig. 1c. The width in $z$ appears broader than the width in $x$.
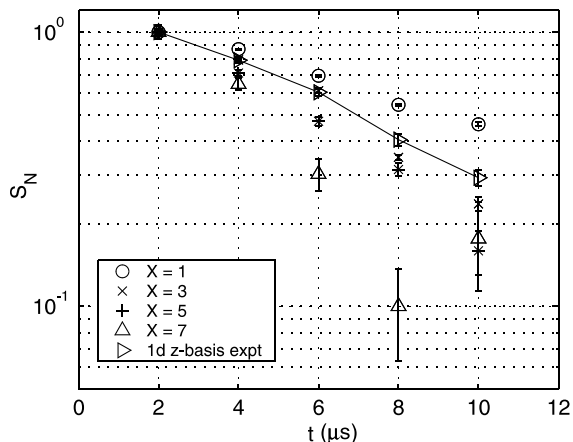


Fig. 5. Decay of the $z$ basis zero quantum signal under the dipolar Hamiltonian. The decay of the different $x$ basis contributions to the zero quantum signal in the $z$ basis, obtained from the 2D experiment are also shown. The data were normalized to the observed intensity at 2 μs. Note that the data are plotted on a log scale. The preparation time used was $\tau = 130.3$ μs, corresponding to 3 loops of the 16 pulse cycle in Fig. 1c.

shown on the figure are the various $x$ basis contributions to the $z$ basis zero quantum signal obtained from the 2D data. The decay is clearly

non-exponential. It can be seen that the different $x$ basis terms attenuate at different rates, and that the measured decay of the 1D $z$ basis data represents some sort of average attenuation of all these terms. Thus, this technique allows us to probe the details of spin dynamics beyond the ability of existing techniques. We have also recently used this technique to study the evolution of the spin system following a Jeener–Broekaert pulse pair, and observed the evolution of the system to a dipolar ordered state [28].

## 4. Conclusions

We have shown that by encoding MQ coherences in different bases ($x$ and $z$) additional information about the state of the spin system may be obtained. In particular, $x$ basis encoding could be useful in determining the size of multiple spin correlations under the action of a Hamiltonian that preserves $z$ basis coherence number, but changes the number of spins in the state, such as the secular dipolar Hamiltonian.

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