Chemical Physics 114 (1987) 103–109
North-Holland, Amsterdam

# MULTIPLE QUANTUM NMR EXCITATION WITH A ONE-QUANTUM HAMILTONIAN

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Received 10 November 1986

Excitation of multiple quantum coherence in dipolar coupled spin systems is usually accomplished with a two-quantum multiple pulse sequence which can be time reversed by means of a 90° phase shift. The application of such an excitation scheme to a spin system in thermal equilibrium excites only even orders of multiple quantum coherence. We demonstrate here time reversible pulse sequences that excite all orders of coherence by creating a pure one-quantum average hamiltonian. We also describe pulse schemes which can be used to create pure one- or two-quantum average hamiltonians with variable scaling between +1 and −1. These excitation schemes are relevant to the study of spin clustering by multiple quantum NMR.

## 1. Introduction

It was realized recently that time reversal sequences [1] can considerably simplify some multiple quantum and two-dimensional (2D) experiments [2–11]. Conventionally, a 2D experiment is divided into four periods: preparation, evolution, mixing and detection. If we denote the average hamiltonian over each of these periods of $H^{\mathrm{P}}$, $H^{\mathrm{E}}$, $H^{\mathrm{M}}$ and $H^{\mathrm{D}}$ respectively, the density operator at the beginning of the detection period can be written as

$$\rho(t_{\mathrm{P}}, t_1, t_{\mathrm{M}}, 0) = \mathrm{e}^{-\mathrm{i}H^{\mathrm{M}}t_{\mathrm{M}}}\,\mathrm{e}^{-\mathrm{i}H^{\mathrm{E}}t_1}\,\mathrm{e}^{-\mathrm{i}H^{\mathrm{P}}t_{\mathrm{P}}}\rho(0) \times \mathrm{e}^{\mathrm{i}H^{\mathrm{P}}t_{\mathrm{P}}}\,\mathrm{e}^{\mathrm{i}H^{\mathrm{E}}t_1}\,\mathrm{e}^{\mathrm{i}H^{\mathrm{M}}t_{\mathrm{M}}} \tag{1}$$

and the expectation value of an observable $Q$ at that time is

$$\begin{aligned}\langle Q\rangle(t_{\mathrm{P}}, t_1, t_{\mathrm{M}}, 0) &= \mathrm{Tr}\Big(\mathrm{e}^{-\mathrm{i}H^{\mathrm{M}}t_{\mathrm{M}}}\,\mathrm{e}^{-\mathrm{i}H^{\mathrm{E}}t_1}\,\mathrm{e}^{-\mathrm{i}H^{\mathrm{P}}t_{\mathrm{P}}}\rho(0) \\ &\quad\times \mathrm{e}^{\mathrm{i}H^{\mathrm{P}}t_{\mathrm{P}}}\,\mathrm{e}^{\mathrm{i}H^{\mathrm{E}}t_1}\,\mathrm{e}^{\mathrm{i}H^{\mathrm{M}}t_{\mathrm{M}}}Q\Big) \\ &= \mathrm{Tr}\Big(\mathrm{e}^{-\mathrm{i}H^{\mathrm{E}}t_1}\,\mathrm{e}^{-\mathrm{i}H^{\mathrm{P}}t_{\mathrm{P}}}\rho(0) \\ &\quad\times \mathrm{e}^{\mathrm{i}H^{\mathrm{P}}t_{\mathrm{P}}}\,\mathrm{e}^{\mathrm{i}H^{\mathrm{E}}t_1}\,\mathrm{e}^{\mathrm{i}H^{\mathrm{M}}t_{\mathrm{M}}}Q\,\mathrm{e}^{-\mathrm{i}H^{\mathrm{M}}t_{\mathrm{M}}}\Big).\end{aligned} \tag{2}$$

In the special case

$$\rho(0) = Q$$

and

$$H^{\mathrm{M}}t_{\mathrm{M}} = -H^{\mathrm{P}}t_{\mathrm{P}} \tag{3}$$

this simplifies to

$$\begin{aligned}\langle Q\rangle(t_{\mathrm{P}}, t_1, t_{\mathrm{M}}, 0) &= \mathrm{Tr}\Big(\mathrm{e}^{-\mathrm{i}H^{\mathrm{E}}t_1}\rho'\,\mathrm{e}^{\mathrm{i}H^{\mathrm{E}}t_1}\rho'\Big) \\ &= \sum_{r,s} |\rho'_{rs}|^2\,\mathrm{e}^{-\mathrm{i}\omega_{rs}t_1},\end{aligned} \tag{4}$$

where

$$\begin{aligned}\rho' = \rho(t_{\mathrm{P}}) &= \mathrm{e}^{-\mathrm{i}H^{\mathrm{P}}t_{\mathrm{P}}}\rho(0)\,\mathrm{e}^{\mathrm{i}H^{\mathrm{P}}t_{\mathrm{P}}} \\ &= \mathrm{e}^{\mathrm{i}H^{\mathrm{M}}t_{\mathrm{M}}}Q\,\mathrm{e}^{-\mathrm{i}H^{\mathrm{M}}t_{\mathrm{M}}}\end{aligned}$$

and

$$\omega_{rs} = H^{\mathrm{E}}_{rr} - H^{\mathrm{E}}_{ss}. \tag{5}$$

All matrix elements are evaluated in the eigenbase of $H^{\mathrm{E}}$. The signal observed as a function of $t_1$ is thus given by the sum of the absolute squares of the density operator elements and therefore independent of any phase factor [2]. This eliminates destructive interference of degenerate transitions by adding the power spectra of all the individual transitions of the system. This is a convenient property in multiple quantum (MQ) NMR where the phases of the individual transitions are a complicated function of the preparation of the spin systems and the information associated with them cannot be easily retrieved. The conventional approach to this problem, calculating absolute value spectra, does not eliminate destructive interference and the associated loss of sensitivity. This is a crucial problem in solids where the number of transitions becomes virtually infinite, leading to a loss of signal due to destructive interference between overlapping transitions with different phases. The problem is illustrated schematically in fig. 1.

The hamiltonians $H^{\mathrm{P}}$ and $H^{\mathrm{M}}$ are usually average hamiltonians generated by an appropriate multiple pulse sequence [12]. The sequences which have been used for multiple quantum NMR in solids [13,14] create a zero-order average dipole–dipole hamiltonian

$$\bar{H}^{(0)}_{2,2} = \tfrac{1}{3}(H_{yy} - H_{xx}) = (d/2)(I_{1+}I_{2+} + I_{1-}I_{2-}), \tag{6}$$

where

$$H_{\alpha\alpha} = d(3I_{1\alpha}I_{2\alpha} - \boldsymbol{I}_1 \cdot \boldsymbol{I}_2) \tag{7}$$

and $d$ represents the dipole–dipole coupling constant. This average hamiltonian has very simple transformation properties under phase shifts:

$$e^{-i\phi I_z}\bar{H}(0)\, e^{i\phi I_z} = 2d\left(e^{2i\phi}I_{1+}I_{2+} + e^{-2i\phi}I_{1-}I_{2-}\right). \tag{8}$$

$H_{yy} - H_{xx}$ thus represents a pure two-quantum operator which changes sign under a phase shift of 90°. The spin system can therefore be forced to evolve backward in time, fulfilling condition (3) by shifting the phase of the multiple pulse sequence. However, such a double-quantum hamiltonian will excite only even orders of coherence for a system in thermal equilibrium in high field.

## 2. One-quantum average hamiltonian

A spin system in thermal equilibrium, represented by the density operator

$$\rho(0) = \sum_i I_{iz} \tag{9}$$

in the high-temperature–high-field limit, does not show any correlations between the individual spins and its density operator is invariant under phase shifts. It consists therefore of 1-spin-0-quantum

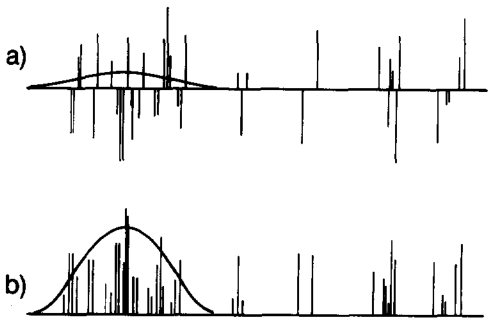

Fig. 1. If the excitation and detection schemes are independent, the phases of the individual transitions are random (a), leading to destructive interference and low signal intensity if the individual transitions are not resolved. With conjugate detection (b) all lines appear in positive absorption, eliminating destructive interference.

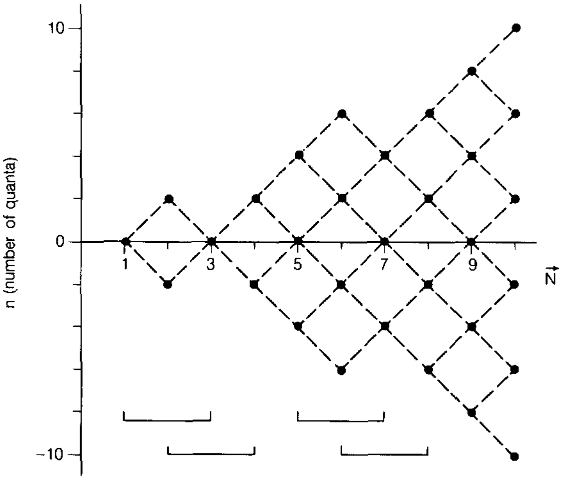

Fig. 2. Possible quantum numbers for $N$-spin operators after excitation with a 2-spin–2-quantum average hamiltonian. The allowed values are for $N$ even: $m = \mp 2, \mp 6, \mp 10, \ldots$, and for $N$ odd: $m = 0, \mp 4, \mp 8, \ldots$, $|m| \leqslant N$. Clearly there are two infinite series of $n$-values with the same possible quantum numbers.

operators. Under the influence of the two-spin operator $H_{yy} - H_{xx}$, correlations develop and the density operator at later times contains $N$-spin-$m$-quantum operators with $N$ and $m$ arbitrarily large. However, there are certain conditions which restrict the possible values of $m$ for a given $N$-spin operator [5]. For spins $I = 1/2$, the magnetic quantum number $m$ is confined to the range

$$-N \leqslant m \leqslant N, \qquad (10)$$

independent of the pulse sequence. In addition, with the above average hamiltonian, only the following values can be obtained:

$$N \text{ even:} \quad m = \mp 2, \mp 6, \mp 10, \ldots, |m| \leqslant N;$$
$$N \text{ odd:} \quad m = 0, \mp 4, \mp 8, \ldots, |m| \leqslant N. \qquad (11)$$

The scheme is represented in fig. 2 [6,7]. Clearly the same sets of $m$-value occur for different values of $N$. In fact, there are two infinite series of $N$-spin operators that show the same pattern:

$$N_1 = 4K + 1 \quad \text{and} \quad N_1' = 4K + 3;$$
$$N_2 = 4K + 2 \quad \text{and} \quad N_2' = 4K + 4,$$
$$K = 0, 1, 2, \ldots. \qquad (12)$$

It has been shown that the pattern and time dependence of multiple quantum intensities can be used to distinguish between different distributions and clustering of spin systems [10]. If the clusters are small, then the excitation of only even orders of coherence is a disadvantage. For these experiments it would be desirable to have a pulse sequence which excites all orders of multiple quantum transitions, providing a more sensitive measure of the cluster size. One possibility is to use a pulse sequence which produces a pure 2-spin-1-quantum average hamiltonian. Such an operator is, up to a rotation about the $z$-axis, given by

$$\bar{H}_{2,1}^{(0)} = d'(I_{1z}I_{2x} + I_{1x}I_{2z}), \qquad (13)$$

where $d'$ is proportional to the unperturbed coupling constant $d$. This can be accomplished by the pulse sequences in fig. 3. The repetitive part of these sequences consists of a cycle of two, four or eight 90° pulses with phase $\pm x$ that generate a zero-order average hamiltonian

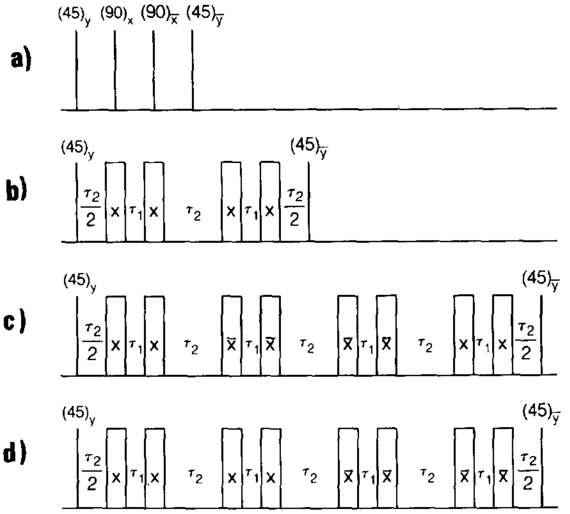

Fig. 3. Pulse sequences that generate 2-spin-1-quantum average hamiltonians. The cycle itself consists only of the $90_x$ and $90_{-x}$ pulses while the $45_y$ and $45_{-y}$ pulses are applied only at the beginning and at the end of the whole sequence. They are therefore not part of the cycle and can be treated as $\delta$-function pulses. The average dipole-dipole hamiltonian is in all cases $(d/3)(I_{1z}I_{2x} + I_{1x}I_{2z})$. (a) This sequence works only in the limit of ideal delta-function pulses and has a non-zero average offset hamiltonian. (b) For this sequence the zero-order average offset hamiltonian vanishes. The delays $\tau$ and $\tau'$ are related by $\tau_2 = 2\tau_1 + t_p$ where $t_p$ is the length of the 90° pulses. This pulse sequence can also be used in a semi-windowless way where $\tau_1 = 0$. (c), (d) These sequences generate zero overall rotation and are therefore less sensitive to pulse errors. The timing is the same as for sequence (b).

$$\bar{H}_{2,1}^{(0)\prime} = d'(I_{1z}I_{2z} - I_{1x}I_{2x}). \qquad (14)$$

The 45° $\pm y$ pulses are not part of the cycle, but are added only once at the beginning and at the end of the whole sequence which may include an arbitrary number of cycles. Their objective is to rotate the average hamiltonian of eq. (14) into its desired form (13). The cycle of the simplest sequence, fig. 3a, consists of only two 90° pulses with opposite phase. The average of the dipole-dipole hamiltonian already has the desired property, but the average of the Zeeman hamiltonian,

$$\bar{H}_Z^{(0)} = \Delta\omega\left[\sqrt{2/3}\,(I_x + I_z) - \tfrac{1}{3}I_y\right], \qquad (15)$$

does not vanish. The performance of this sequence is therefore strongly offset-dependent. Furthermore it works only with ideal delta-function pulses. The simplest sequence with the same average dipole–dipole hamiltonian and a vanishing Zeeman hamiltonian has a cycle of four 90° pulses with equal phases, fig. 3b. The delays are related by $\tau_2 = 2\tau_1 + t_p$. This sequence works equally well with finite pulse width, and may therefore be used in a semi-windowless manner [15,16]. The net rotation of this sequence is $2\pi$ so that pulse errors accumulate. It is more useful in practice to use one of the longer sequences of figs. 3c and 3d. They can also be used in the semi-windowless manner.

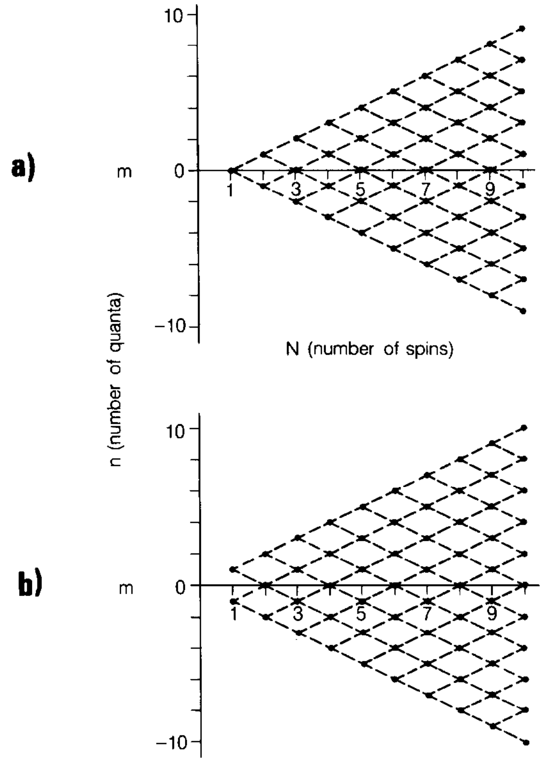

Fig. 4. (a) Possible quantum numbers for $N$-spin operators after excitation with a 2-spin–1-quantum operator and initial condition $I_z$. The allowed values are for $N$ even: $m = \mp 1, \mp 3, \mp 5, \ldots$, and for $N$ odd: $m = 0, \mp 2, \mp 4, \ldots, |m| \leqslant N$. (b) Same with 1-spin–1-quantum operators as the initial condition, e.g. $I_x$. The allowed values are for $N$ even: $m = 0, \mp 2, \mp 4, \ldots$, and for $N$ odd: $m = \mp 1, \mp 3, \mp 5, \ldots, |m| \leqslant N$.

The possible values of the magnetic quantum number $m$ for $N$-spin operators generated by these average hamiltonian from spin systems at equi-

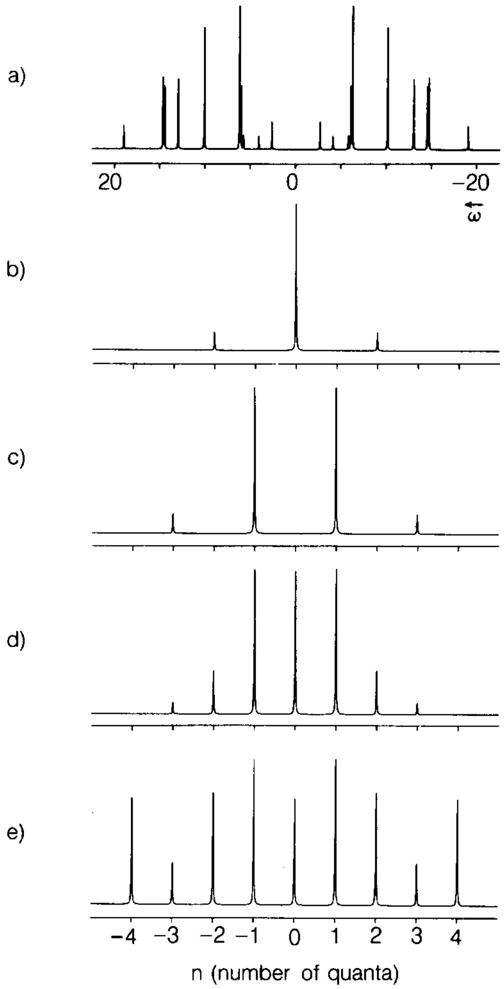

Fig. 5. (a) Simulated single quantum spectrum for an $AA'BB'$ spin system with the coupling constants $d_{12} = d_{34} = 6.25$ kHz, $d_{13} = d_{24} = -0.24$ kHz, $d_{14} = -0.625$ kHz and $d_{23} = -5$ kHz. (b) Calculated multiple-quantum intensities for the same spin system using the even-order selective sequence and an excitation time $\tau_p = 100$ μs. Initial condition and observable are both $I_z$. Apparently it is not possible to distinguish this system from a two-spin system only by measuring the multiple quantum intensities. (c) As (b), but with initial condition and observable set to $I_x$. In this case only odd orders are observed. (d) As (b), but using the sequence of fig. 3c. Initial condition and observable are $I_z$. (e) As (d), but the initial condition and observable set to $I_x$. Only under these conditions is the highest-order transition excited.

librium are shown in fig. 4a. Clearly the sequences never excite the highest-order transitions, but all $N$-spin operators are of order $m \leqslant N-1$. This is due to the initial condition of $I_z$ which is a 1-spin–0-quantum operator. The highest possible transition can be excited by changing the initial condition and the observable to $I_x$, a 1-spin–1-quantum operator, e.g. by a $90_y$ pulse, as shown in fig. 4b. Fig. 5 shows a computer simulation for various excitation schemes, applied to a system of four spins 1/2. If the even quantum selective sequence is used with initial condition $I_z$, it is not possible to distinguish this system from a two-spin system by looking only at the multiple quantum intensities. This becomes possible by using $I_x$ as an initial condition. The two spectra, figs. 5b and 5c, together are roughly equivalent to the single spectrum, fig. 5d, obtained with the one quantum sequence of fig. 3d. The highest orders can be excited only with this sequence and the initial condition $I_x$, as shown in fig. 5e.

Fig. 6 shows experimental multiple quantum spectra of solid hexamethylbenzene. The comparison of the two sequences shows that the single quantum sequence leads to a slower excitation of higher quanta, but with a more sensitive measure of multiple quantum intensity distribution at short times.

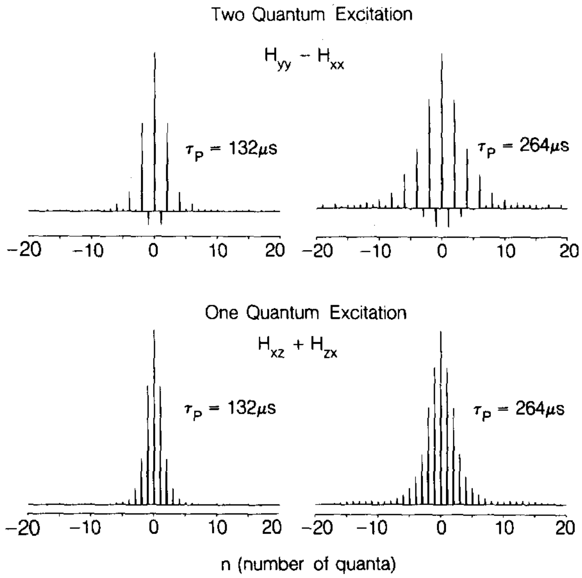

Fig. 6. Experimental spectra of hexamethylbenzene. The top spectra were obtained with the even quantum selective sequence. Excitation times were 132 μs (2 cycles) and 264 μs (4 cycles). The bottom spectra were obtained with the sequence of fig. 3c.

## 3. One- or two-quantum average hamiltonian with scaling

A problem which occurs with both the one-quantum and two-quantum average hamiltonian is the limit on short-time resolution of multiple quantum excitation dynamics. The system must be excited in steps of $H^{\mathrm{P}}\tau_{\mathrm{c}}$ where $\tau_{\mathrm{c}}$ represents the cycle time of the pulse sequence. If smaller excitation steps are required to look at the early dynamics then either $\tau_{\mathrm{c}}$ must be reduced or a smaller $H^{\mathrm{P}}$ must be implemented without increasing the cycle time. Reduction of $\tau_{\mathrm{c}}$ is obviously limited by experimental considerations such as power. It is therefore desirable to design a pulse sequence that implements an average hamiltonian with a smaller effective coupling constant. Such an average hamiltonian effectively slows down the evolution of the spin system while maintaining the one- or two-quantum nature and the possibility of time reversal by phase shift.

Pulse cycles for such scaled average hamiltonian with one- or two-quantum selectivity can be derived from the sequence $(b\text{–}90_x\text{–}(a-t_{\mathrm{p}}/2)\text{–}90_y\text{–}2c\text{–}90_y\text{–}(a-t_{\mathrm{p}}/2)\text{–}90_x\text{–}2b\text{–}90_x\text{–}(a-t_{\mathrm{p}}/2)\text{–}90_y\text{–}2c\text{–}90_y\text{–}(a-t_{\mathrm{p}}/2)\text{–}90_x\text{–}b)$, shown in fig. 7), where $a$, $b$ and $c$ represent adjustable delays and $t_{\mathrm{p}}$ the duration of a 90° pulse. This sequene generates a zero-order average hamiltonian

$$\begin{aligned}\overline{H}^{(0)} = {} & d\left(a+b+c+3t_{\mathrm{p}}/2\right)^{-1} \\ & \times\left[I_{1x}I_{2x}(2c-b-a)\right. \\ & +I_{1y}I_{2y}(2a-b-c) \\ & \left.+I_{1z}I_{2z}(2b-a-c)\right]. \end{aligned} \tag{16}$$

The zero-order average hamiltonian of the offset vanishes. Eq. (16) shows that it is possible to generate pulse sequences with a pure two-quan-

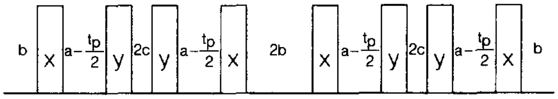

Fig. 7. Basic pulse sequence for pure $n$-quantum average hamiltonians with scaled effective coupling strength. The effective coupling constant can be chosen by setting the delays $a$, $b$ and $c$ appropriately (see text). With the timing of the pulses as shown, the sequence generates a pure two-quantum average hamiltonian with an effective coupling constant scaled by a factor $-1/2$.

tum average hamiltonian if

$$b=(a+c)/2. \tag{17}$$

The average hamiltonian of the sequence then becomes

$$\bar{H}^{(0)2Q}=d\left[(c-a)/(c+a+t_p)\right] \times\left(I_{1x}I_{2x}-I_{1y}I_{2y}\right). \tag{18}$$

Thus the effective coupling constant can be scaled by a factor which varies between $+1$ and $-1$. For $c=a$, the average hamiltonian becomes zero and the resulting pulse sequence is identical to the SHRIMP sequence [17]. Because the effective coupling constant can be varied through zero, this sequence can be used for time-reversal experiments not only by adjusting the transmitter phase, but alternatively by changing the length of the delays between the pulses.

The corresponding one-quantum selective sequences can be obtained via the same indirect procedure as was used for the unscaled sequences. We first require $H_{yy}$ to vanish by setting

$$a=(b+c)/2, \tag{19}$$

which leads to an average hamiltonian

$$\bar{H}^{(0)1Q}=d\left[(c-b)/(c+b+t_p)\right] \times\left(I_{1x}I_{2x}-I_{1z}I_{2z}\right), \tag{20}$$

which can then be converted into the desired one-quantum operator by adding a $45_y$ pulse at the beginning and a $45_{-y}$ pulse at the end of the whole sequence. Again, the effective coupling constant can be scaled from $+1$ to $-1$ by adjusting the length of the delays. We use the names SQUASH (single quantum average scaled hamiltonian) and DQUASH (double quantum average scaled hamiltonian) for these sequences.

The sequences derived from the scheme of fig. 7 are more susceptible to pulse length errors than the standard sequence [14]. If inhomogeneity of the radiofrequency field becomes an experimental problem, it may therefore be advantageous to minimize errors by using only one cycle of the scaling sequence in the preparation and mixing period to get the desired value of $H^{\mathrm{P}}\tau_{\mathrm{c}}$.

## 4. Conclusions

Dipolar coupled spin systems can be made to absorb quanta from the radiation field either individually or in pairs and can be made to undergo multiple quantum dynamics which can be slowed down, stopped or inverted by adjusting the phases and the delays of the pulse sequence. The sequences presented in this paper should be useful for the study of spin dynamics in small clusters where the interesting time evolution occurs over a relatively short time and it is a pity to lose the additional resolution provided by the odd quantum transitions. They also make it possible to observe the highest possible $n$-quantum transition in a spin cluster of any size. For large spin systems, however, it may still pay to use the even quantum selective sequence. The intensities are distributed among a smaller number of transitions and the excitation of high quanta occurs more rapidly.

## Acknowledgement

We greatfully acknowledge experimental assistance by D.N. Shykind. JB held a University of California President's Fellowship. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-Ac03-76SF00098.

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