Journal of Magnetic Resonance **141,** 322–325 (1999)
Article ID jmre.1999.1890, available online at http://www.idealibrary.com on IDEAL®

Efficient Refocusing of One-Spin and Two-Spin Interactions for NMR Quantum Computation

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Received May 7, 1999; revised July 20, 1999

The use of spin echoes to refocus one-spin interactions (chemical shifts) and two-spin interactions (spin–spin couplings) plays a central role in both conventional NMR experiments and NMR quantum computation. Here we describe schemes for efficient refocusing of such interactions in both fully and partially coupled spin systems. © 1999 Academic Press

Key Words: **spin echo; hadamard; quantum computation; graph; proper coloring.**

I. INTRODUCTION

Much of the power and utility of NMR stems from the ease with which the experimenter can control the effective Hamiltonian experienced by the spin system. In conventional NMR (*1*) this permits different interactions to be studied individually, while in NMR quantum computation (*2–5*) this process is used to generate Hamiltonians corresponding to quantum logic gates between specific spins (*6*). This manipulation can be achieved using a variety of techniques (*7*), but the simplest and most important approach is the use of spin echoes. Applying a 180° pulse to a single spin in the middle of some evolution period acts to refocus any evolution occurring as a result of one-spin interactions (that is, chemical shifts) or two-spin interactions (spin–spin coupling, assumed to be *weak*) involving that spin. Thus the corresponding terms in the spin Hamiltonian are effectively deleted.

This approach is simple to apply in systems containing only a small number of coupled spins, but must be treated with caution when applied to larger systems, especially when all the spins are coupled to one another. The Hamiltonian describing evolution of a fully coupled spin system of N spins contains N one-spin terms and $N(N-1)/2$ two-spin terms, and it would be possible to produce a large number of effective Hamiltonians, corresponding to any desired combination of these terms. For simplicity we will concentrate on one particularly simple Hamiltonian in which only one chemical shift term is retained; two other simple Hamiltonians (in which only one coupling is retained or all interactions are refocused) can be easily generated by small modifications to the corresponding pulse sequences.

A pulse sequence for achieving this simplification in a two-spin system is shown in Fig. 1. In this case the refocusing process is simple and can be achieved with only two time periods, separated by a single 180° pulse. For completeness it is necessary to apply a final 180° pulse to spin 1 to ensure that each spin experiences an even number of 180° pulses (NOT gates), but in many cases such pulses can be omitted. When applied to larger spin systems, however, it is necessary to refocus many more interactions, requiring a larger number of time periods. The conventional approach (*8*) is to recursively nest copies of sequences like that shown in Fig. 1 within one another, as shown for a fully coupled four-spin system in Fig. 2. While this nesting process is effective, it is exponentially inefficient, in that the number of time periods and 180° pulses required grows exponentially with the number of spins in the spin system: while a four-spin system requires that the evolution period be divided into 8 sections, a five-spin system will require 16 sections, and so on.

Although this nesting process is very widely used within NMR, a far more efficient scheme is available. Here we describe this efficient refocusing scheme and show how it may be used to create the two effective Hamiltonians described above (*9*). We also discuss the application of this scheme to partially coupled spin systems and some practical issues arising from its application in homonuclear systems.

II. THEORY

While spin echo sequences are usually drawn out as sequences of pulses, as shown above, it is more convenient to describe a sequence mathematically by considering the evolution of each spin during the various equal time periods of free precession (the 180° pulses are assumed to be of negligible duration). Suppose that before the start of the spin echo sequence a spin is in a state of $p = +1$ quantum coherence; the effect of the 180° pulse is to convert this to -1 quantum coherence, and vice versa. The evolution of the spin will

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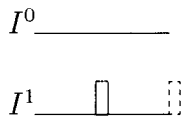

FIG. 1. Pulse sequence for generating a simple effective Hamiltonian in a two-spin (I^0 and I^1) system; boxes correspond to 180° pulses. This sequence generates the Hamiltonian corresponding to the chemical shift of spin 0 (I_z^0); the final 180° pulse, shown as a dashed box, can often be omitted.

depend on its coherence order, and thus the evolution during any period can be described by a set of numbers taking the values $+1$ and -1, where the value changes sign each time a 180° pulse is applied to the spin.

These sets of values can then be gathered together into a matrix, whose rows correspond to the individual spins and whose columns correspond to the different time periods. Thus the sequence depicted in Fig. 1 can be described by the matrix

$$M_2 = \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}, \qquad [1]$$

while that shown in Fig. 2 corresponds to the matrix

$$M_4 = \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 \\ 1 & 1 & -1 & -1 & -1 & -1 & 1 & 1 \\ 1 & -1 & -1 & 1 & 1 & -1 & -1 & 1 \end{pmatrix}. \qquad [2]$$

The refocusing effected by these pulse sequences can then be easily explained by examining the properties of the corresponding matrices. The chemical shift of a spin will be refocused as long as the corresponding row of the matrix M contains the same number of plus and minus ones. Similarly the (weak) coupling between two spins will be refocused if the vector obtained by multiplying pairs of numbers from the rows corresponding to the two spins contains the same number of plus and minus ones. More concisely, a spin–spin coupling will be refocused if the corresponding rows are orthogonal, while a chemical shift will be refocused if the corresponding row is orthogonal to a row of ones.

These two properties are sufficient to allow us to construct refocusing matrices, and thus pulse sequences, with the desired properties. Consider a system of N spins, where we wish to refocus all the interactions *except* the chemical shift of spin 0. This can be achieved by constructing a refocusing matrix comprising one row of ones and $N - 1$ rows of plus and minus ones, all of which are orthogonal to one another and to the first row; the most efficient refocusing sequence will correspond to the matrix with the smallest number of columns. Such matrices are closely related to the well-known Hadamard matrices.

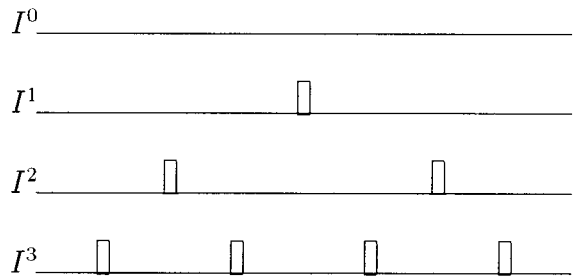

FIG. 2. A pulse sequence for generating the effective Hamiltonian I_z^0 in a fully coupled four-spin system; boxes correspond to 180° pulses.

The Hadamard matrix corresponding to a two-spin system, H_2, takes the simple form

$$H_2 = M_2 = \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}, \qquad [3]$$

and so the conventional two-spin sequence (Fig. 1) is, not surprisingly, the most efficient. The four-spin Hadamard matrix, H_4, can be calculated using

$$H_4 = H_2 \otimes H_2 = \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & -1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & -1 & 1 \end{pmatrix}, \qquad [4]$$

and is only half the size of its conventional equivalent, M_4 (Eq. [2]). The corresponding pulse sequence, shown in Fig. 3, is similarly shorter than the conventional equivalent (Fig. 2). Note that, with the exception of spin 0, there is no particular significance to the spin labels, and individual nuclei can be assigned to the different spin numbers at will.

Unlike conventional spin echo sequences, these efficient sequences involve the application of simultaneous 180° pulses to two or more spins. In principle this need not be a problem, but in practice it may be necessary to choose B_1 field strengths with care, so as to minimize the effects of Hartmann–Hahn transfers (whether homonuclear or heteronuclear). Practical issues of this kind are discussed in more detail below.

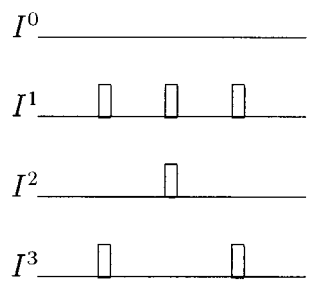

FIG. 3. An efficient pulse sequence for generating the effective Hamiltonian I_z^0 in a fully coupled four-spin system.

With slight modifications, these pulse sequences can also be used to generate effective Hamiltonians corresponding to a single spin–spin coupling. The procedure is straightforward: to generate a pure coupling between spins 0 and 1 (for example), simply copy the pulses applied to spin 1 and apply them to spin 0. Similarly, a pulse sequence in which *all* one- and two-spin interactions are refocused in an N spin system can be obtained by using the bottom N lines of a sequence which refocuses everything except the first chemical shift in an $N + 1$ spin system.

The usefulness of this procedure depends on the existence of Hadamard matrices with appropriate dimensions. Ideally the matrix should have the same size as the number of spins in the spin system. Unfortunately it is usually only possible to form Hadamard matrices whose dimension is a multiple of 4 (the 2 by 2 Hadamard matrix, H_2, is a special case); Hadamard matrices can be formed for many (although not all) multiples of 4, including all such multiples below 50 (*10, 11*). When the number of spins is *not* a multiple of 4, it is instead necessary to use the next largest appropriate multiple of 4 and select an appropriate subset of the corresponding pulse sequence. In general this subset would probably be chosen to minimize the number of simultaneous pulses in the pulse sequence. For example, in a three-spin system one possible pulse sequence is to use the lines labeled I^0, I^2, and I^3 in Fig. 3; this choice corresponds to the conventional pulse sequence! This procedure is always more efficient than the conventional approach except for the case of two or three spins: in these cases the conventional and Hadamard approaches give identical sequences.

A discussed below, in real systems where only some of the possible couplings are present it is not necessary to refocus all the couplings, and it is instead possible to use simpler pulse sequences. Spin coupling networks in molecules are usually quite local, with resolved couplings only being seen to a small number of close neighbors; it seems likely that the four-spin (Fig. 3) and eight-spin (Fig. 4) sequences would suffice for almost any system.

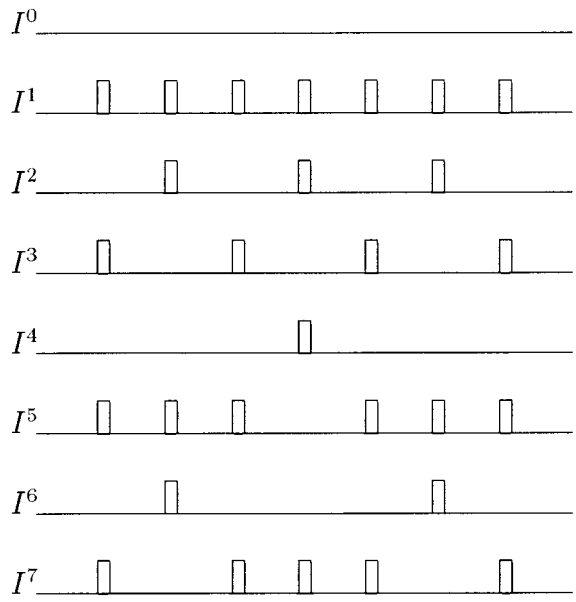

FIG. 4. An efficient pulse sequence for generating the effective Hamiltonian I_z^0 in a fully coupled eight-spin system. The conventional sequence would require 127 pulses distributed over 128 delay periods.

III. PARTIALLY COUPLED SPIN SYSTEMS

In real life fully coupled spin systems are rather rare; in most cases only a small subset of the possible couplings can be resolved. It is not necessary to refocus all these unresolved couplings, which are effectively absent, and thus the refocusing process can be greatly simplified. In small spin systems it is practical to derive such simplified sequences by hand, but in larger systems it is useful to have an algorithmic procedure by which this can be achieved.

This is simply realized by treating the spin system as a noncomplete graph (*12*). A graph comprises a set of vertices, connected by edges; this corresponds to a set of nuclei connected by J-couplings. A partially coupled spin system, in which some of the couplings are absent, corresponds to a noncomplete graph. A graph can be colored, by assigning each vertex one of a number of different colors, and the coloring scheme is called a proper coloring if no two connected vertices are the same color. The graph may then be characterized by a chromatic number, χ: this is the smallest number of colors required to properly color the graph. In a complete graph (a fully coupled spin system) $\chi = N$, but in a partially coupled system χ can be much smaller.

The significance of this observation is that if a spin system is represented by a properly colored graph, then it is not necessary to refocus interactions between nuclei corresponding to vertices with the same color. To refocus all the interactions in an N spin system it suffices to create a pulse sequence corresponding to a χ spin system and apply identical pulses to all nuclei with the same color. In this case there is no need for further concern about Hartmann–Hahn transfers, as these additional simultaneous pulses will only be applied to spins which are not coupled to one another.

Clearly this approach is only practical if it is easy to determine both the value of χ and a corresponding proper coloring. In general this is extremely difficult: indeed, determining χ is an NP hard problem. This difficulty is, however, more apparent than real, as it is relatively simple to estimate χ and to find corresponding proper colorings, for certain simple types of graph such as those likely to occur in coupled spin systems. If the maximum number of edges at any vertex (that is, the maximum number of spins coupled to any other spin) is k, then the graph is said to be of degree k, and $\chi \leq k + 1$; in all but a few special cases $\chi \leq k$. Furthermore, it is easy to construct a proper coloring using at most k (or $k + 1$) colors. Creating a sequence which refocuses all interactions except one chem-

ical shift or one J-coupling is slightly more complicated, but the simplest approach is to assign the nuclei in question a unique color; at worst this will increase the number of colors required by 1.

IV. PRACTICALITIES

The sequences described above can be immediately applied to fully heteronuclear spin systems. In this case the assumption of weak couplings is good, and it is possible to implement spin-selective pulses using short hard pulses. Unfortunately this approach cannot be applied very far, as the number of suitable spin-$\frac{1}{2}$ nuclei available is small, and so it is not possible to simply use a different nucleus for each qubit.

With homonuclear systems it is necessary to apply our approach with care. Spin-selective excitation will now require the use of long soft pulses, and it may not be possible to fit all the pulses within the time required for evolution under the spin–spin coupling (typically given by the antiphase condition). In such cases it is necessary to extend the length of the sequence by using the second or later antiphase condition. Of course such problems will be even more severe with conventional refocusing sequences, as these require a larger number of pulses and evolution periods. There are, however, additional problems when using our new approach with homonuclear systems which do not occur with conventional refocusing sequences; these arise from the use of simultaneous soft pulses on two or more nuclei. When simultaneous pulses are applied to two coupled nuclei, and the length of the pulses is significant in comparison with the inverse of the spin–spin coupling, two-spin effects can occur (*7, 13*), giving rise to coherence transfer. Even when two nuclei do not have a significant coupling, it may be difficult to apply simultaneous soft pulses to them as a result of "collisions" between the two soft pulses, although these effects can be reduced by the use of time-reversed pulses (*7, 14*).

The problems described above might seem so severe as to render this approach impossible in homonuclear spin systems, but in fact this is unlikely to be the case. These effects will only be severe in systems containing a large number of closely spaced resonances, such as spin systems made up solely of ^{1}H nuclei. In more realistic systems containing a mixture of spins, including nuclei such as ^{13}C and ^{19}F which have wide chemical shift ranges, it should be possible to apply these new refocusing sequences without severe problems.

V. CONCLUSIONS

The use of Hadamard matrices and noncomplete graphs provides a powerful language for describing pulse sequences which refocus one-spin and two-spin interactions in NMR. This approach permits the construction of refocusing pulse sequences which are much shorter than their conventional equivalents. However, some care must be taken when applying this approach to homonuclear spin systems.

ACKNOWLEDGMENTS

We thank M. Mosca for useful discussions. J.A.J. is a Royal Society University Research Fellow. E.K. thanks the National Security Agency for financial support. J.A.J. thanks Starlab (Riverland NV, Belgium) for support.

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