Pulse Sequences for NMR Quantum Computers: How to Manipulate Nuclear Spins While Freezing the Motion of Coupled Neighbours

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Abstract

We show how to divide a coupled multi-spin system into an small subset of “active” spins that evolve under chemical shift or scalar coupling operators, and a larger subset of “spectator” spins which are returned to their initial states, as if their motion had been temporarily frozen. This allows us to implement basic one-qubit and two-qubit operations from which general operations on $N$-qubits can be constructed, suitable for quantum computation. The principles are illustrated by experiments on the three coupled protons of 2,3-dibromopropanoic acid, but the method is applicable to any spin-$1/2$ nuclei and to systems containing arbitrary numbers of coupled spins.

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1 Introduction

In this letter we address the problem of how to use NMR techniques to manipulate subsets of spins in a multi-spin system while leaving the states of all the other coupled spins unchanged. We have in mind the use of these manipulations to generate pulse sequence modules which will be useful for NMR quantum computation [1, 2, 3, 4, 5, 6, 7, 8, 9].

This leads to an important difference of emphasis from conventional NMR spectroscopy where one can assume that the states of the spins before the manipulation are known, and indeed one often arranges these states (for example as $z$-magnetization) so that the manipulation has a simple effect on the spins. One is certainly not concerned about the effect that the pulse sequence might have on the spins. One is certainly not concerned about the effect that the pulse sequence might have on the spins. One is certainly not concerned about the effect that the pulse sequence might have on the spins.

Furthermore, one is typically only interested in the effect of the manipulation on a subset of the spins and it is irrelevant how the other spins evolve. In contrast, in applications to NMR quantum computing, the state of the system before the given pulse sequence module is assumed unknown. The module is a logic gate which is designed to carry out a specified unitary transformation which can be applied to any input, the remaining qubits must remain passive spectators.

A system of $N$ spins evolves under a Hamiltonian which includes chemical shifts for each spin and scalar coupling terms for every pair of spins. Thus if one wishes to manipulate a particular spin, and the manipulation is not effectively instantaneous, all the other spins will evolve, in a complicated, coupled, manner. We will show here how to apply patterns of pulses so that only the desired chemical shifts and scalar couplings affect the evolution of the system as if we had “switched off” all the other terms in the Hamiltonian. For example, we will show how to produce pulses whose net effect is to allow only one spin to precess under its chemical shift: no matter what the input states of the other spins are, at the end of the pulse sequence they will be returned to their initial states.

For concreteness we will use a weakly-coupled three spin ($ISR$) system to demonstrate the theoretical and experimental results. This system has the “free” Hamiltonian (i.e. the Hamiltonian in the absence of pulses) of the form

$$\mathcal{H}_0 = \omega_I I_z + \omega_S S_z + \omega_R R_z + 2\pi J_{IS} I_z S_z + 2\pi J_{IR} I_z R_z + 2\pi J_{SR} S_z R_z.$$  (1)

Using patterns of refocusing pulses we will show how to create unitary operations on the
spin system as if many of the terms in the Hamiltonian were zero. We will demonstrate theoretically and experimentally how to generate three basic operations:

- **O1** Chemical shift evolution of a single spin
- **O2** Rotation of a single spin by an arbitrary angle about a general axis (this generalises O1)
- **O3** Evolution under scalar coupling leading to the two-qubit operation whose product operator representation is \( \exp(i\phi 2I_zS_z) \)

Straightforward generalisations of the sequences will produce analogous modules to O1, O2 and O3 for systems of any number of spins and these modules are sufficient to generate any unitary operation on N qubits. This follows from the important result in [10] that any arbitrary unitary transformation of N spins can be built up from two simple building blocks: these may be taken to be, for example, an arbitrary rotation of a single spin, and the two-qubit operation \( \exp(-i\pi 2I_zS_z) \). The reason for this particular choice of basic operations is that they may easily be generated using the natural evolution of the system. We note that the two-qubit operation \( \exp(-i\pi 2I_zS_z) \), which has matrix representation

\[
e^{-i\frac{\pi}{2}} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & i & 0 & 0 \\ 0 & 0 & i & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix},
\]

is closely related to the controlled-not (CNOT) operation on two qubits.

The first operation O1 is implemented by the pulse sequence given in Fig 1. The sequence of refocussing \( \pi \) pulses on spins R and S creates a unitary evolution of the system as if the only non-zero term in the Hamiltonian were \( \omega I_z \). Thus the effect of the sequence is to act on the complete system with the unitary operator \( e^{i\phi I_z} \). As an example of how the generalisation to N-spins works, consider the case of four spins labelled ISRQ. Evolution of the I spin alone can be arranged during a period of 16\( \tau \) by having \( \pi \) pulses on S at \((8m+4)\tau, m = 0 \ldots 1\), on R at \((4m+2)\tau, m = 0 \ldots 3\), and on Q at \((2m+1)\tau, m = 0 \ldots 7\).

Returning to the ISR system, we see that we can convert the phase evolution sequence (a rotation about the z axis) into a general excitation pulse O2. The I-spin magnetization
may be rotated through an angle $\phi$ about a tilted axis in the $xz$ plane by enclosing the unitary operator $e^{i\phi I_z}$ between two hard pulses applied along the $-y$ and $+y$ axes:

$$e^{-i\beta(I_y+S_y+R_y)} e^{i\phi I_z} e^{+i\beta(I_y+S_y+R_y)},$$

(3)

the hard pulses are effectively instantaneous so that no evolution under $H_0$ takes place. This tilts the rotation axis away from $+z$ through an angle $\beta$ in the $xz$ plane. The rotation can be made completely general by enclosing sequence (3) between two $z$-rotation O1 modules:

$$e^{-i\gamma I_z} e^{-i\beta(I_y+S_y+R_y)} e^{i\phi I_z} e^{+i\beta(I_y+S_y+R_y)} e^{+i\gamma I_z}.$$  

(4)

Rotation now takes place about a tilted radiofrequency field in a vertical plane that subtends an azimuthal angle $\gamma$ with respect to the $+x$ axis. As a specific example we will demonstrate experimentally the case $\phi = \pi$, $\beta = \pi/4$, $\gamma = 0$.

The final basic operation is the two-qubit operation O3. The sequence of refocussing pulses is given in Fig 2. We note that this sequence, together with the previous ones, can be used to create the unitary operation whose total effect is to perform a CNOT operation between $I$ and $S$ (with the $R$ spin unaffected). Recall that the effect of O3 is, in terms of product operators, $\exp(i\phi 2 I_z S_z)$. The CNOT operation on two spins may be represented by the unitary matrix

$$U_{\text{CNOT}} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}.$$  

(5)

The corresponding product operator representation is

$$U_{\text{CNOT}} = e^{-i\frac{\pi}{4}} e^{+i\frac{\pi}{2} I_z} e^{i\frac{\pi}{2} I_x} e^{-i\frac{\pi}{2} I_x} e^{+i\frac{\pi}{2} I_y} e^{+i\gamma I_z}.$$  

(6)

It can be seen that each term in the product (except for the irrelevant overall phase) can be created using O1, O2 or O3.

Thus the pulse sequences we describe in this letter give us a set of basic modules which are sufficient to produce an arbitrary unitary operation on a system of 3 qubits. In
practice there may be more straightforward pulses which suggest themselves as NMR implementations of the essential parts of given gates. However there are often “corrections” which need to be made to implement the exact unitary operator required [2, 9]. Consider for example the controlled-controlled-not (CCNOT) gate on three qubits:

\[
U_{\text{CCNOT}} = \begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1
\end{pmatrix}.
\] (7)

This may be implemented with a sequence of five controlled rotations [10]. However using a line-selective pulse it is straightforward to generate the key part of this gate [9], giving the unitary operator

\[
\tilde{U}_{\text{CCNOT}} = \begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & i
\end{pmatrix}.
\] (8)

It is not difficult to show that

\[
U_{\text{CCNOT}} = e^{i\frac{\pi}{4}I_z+i\frac{\pi}{4}S_z-i\frac{\pi}{2}I_zS_z} \tilde{U}_{\text{CCNOT}},
\] (9)

up to an irrelevant overall phase. Thus the exact unitary operation required, \(U_{\text{CCNOT}}\), can be implemented by performing \(\tilde{U}_{\text{CCNOT}}\) followed by a sequence of corrections of the type we describe in this letter.

2 Experimental realization

We take as representative practical example a homonuclear weakly-coupled three-spin (ISR) system where all three coupling constants \(J_{IS}, J_{IR}\) and \(J_{RS}\) are non-zero and
resolvable. Relaxation effects (spin-spin and spin-lattice relaxation and the nuclear Overhauser effect) are specifically excluded from the discussion since they change intensities in an irreversible manner; of course if the pulse sequences have appreciable duration, relaxation effects will be observed. Multiplet-selective radiofrequency refocusing pulses are employed in a symmetrical arrangement to refocus the appropriate chemical shifts and spin-spin splittings. An essential property of these soft pulses is that they should act as “universal rotors”, that is to say, within their effective bandwidth, they induce the same rotation whatever the initial state of the nuclear magnetization. Gaussian shaped pulses do not satisfy this requirement; instead time-symmetric, shaped radiofrequency “RE-BURP” pulses are used. These refocusing “π” pulses are never applied to two different nuclear spins simultaneously, since that would introduce spin-echo modulation through the scalar coupling and create multiple-quantum coherence through the double-resonance two-spin effect (TSETSE). The refocusing pulses are employed in a sequence designed to take advantage of the fact that radiofrequency pulse imperfections are corrected on even-numbered spin echoes.

Experiments were carried out at 22°C on a Varian 400 MHz high-resolution spectrometer on the three coupled protons (R, I and S) in 2,3-dibromopropanoic acid dissolved in benzene-d$_6$, where $J_{IS} = -10.1$ Hz, $J_{IR} = 11.3$ Hz, $J_{RS} = 4.3$ Hz, $\delta_{IR} = 188.5$ Hz and $\delta_{IS} = 219.5$ Hz. After removal of dissolved oxygen by bubbling argon through the solution, the measured spin-lattice relaxation times were 9.5 s (R) and 1.8 s (I and S). Although this particular homonuclear system provides a simple example to demonstrate the principles involved, it is not ideal for the purpose. The chemical shift differences are rather small, placing heavy demands on the selectivity of the soft π pulses, the uniformity of excitation across a chosen spin multiplet, and the effectiveness of the suppression off-resonance. Some strong coupling effects are also evident, particularly between spins R and I. Analogous experiments on heteronuclear systems (or on homonuclear carbon-13 systems) would be expected to pose fewer practical problems. Selectivity would no longer be crucial, and because the pulses would be of much shorter duration, relaxation and coupling effects during the pulses could be safely neglected.
2.1 Module O1: Selective phase evolution

The basic module O1 is designed to refocus the spin-spin splittings of the active (I) spin but allow chemical shift evolution to accumulate a phase shift $\phi$, leaving the coupled spectators $R$ and $S$ unaffected (Fig. 1). After excitation of magnetization by a hard pulse applied about the $x$-axis, the divergence of $I$-spin magnetization trajectories due to $J_{IR}$ and $J_{IS}$ is refocused by soft $\pi$ pulses applied to $R$ and $S$, so that only the chemical shift effect persists. It was found that the effects of pulse imperfections were reduced by applying the two $S$ pulses with the same phase ($+y$) and by setting the phases of the four $R$ pulses to $(+y + y - y - y)$ according to the MLEV-4 prescription [14]. The phase evolution diagram (Fig. 1) illustrates the refocusing process. The $S$ and the $R$ spins remain passive spectators because their chemical shifts and spin-spin splittings are refocused by the $\pi$ pulses, and certain pulse imperfections are compensated by the operation of the $\pi$ pulses acting in pairs [13]. At the end of the sequence the $I$ spins accumulate a phase shift $\phi = 2\pi\delta_I 8\tau$ radians which can be controlled by adjusting either the duration of the sequence ($8\tau$) or the offset $\delta_I$ Hz between the $I$-spin chemical shift and the transmitter frequency.

There is a minor instrumental complication when soft radiofrequency pulses are used in this manner, since each radiofrequency field induces a small Bloch-Siegert shift [15] on neighbouring resonances, always in the direction to move the neighbour resonance away from the irradiation field. This translates into a small additional increment in the phase of the nuclear precession. For the $I$ spins these small phase errors merely accumulate and can be corrected by a slight readjustment of the overall duration of the sequence. For the $S$ spins the symmetry of the sequence is such that these phase errors are effectively refocused by the soft $\pi$ pulses. Unfortunately the perturbation of the motion of the $R$ spins by the pulses applied to $S$ is not refocused. The Bloch-Siegert effect on $R$ was therefore compensated by applying “ghost” $\pi$ pulses at the same time as the $S$ pulses and with the same amplitude and duration, but with the offset from the $R$ resonance reversed in sign. These ghost pulses fall in empty regions of the spectrum, exciting no NMR response directly. With this precaution an experimental test of the $e^{i\phi I_z}$ module gave the spectra illustrated in Fig. 3. The duration of the sequence ($8\tau$) was incremented so that the accumulated phase $\phi$ of the $I$-spin response varied over a range of $2\pi$ radians. Note the
attenuation of the $I$-spin signal due to $T_2^*$ losses over the relatively long durations ($8\tau$ varied between 1.15 and 1.23 seconds), whereas this effect is refocused for the $R$ and $S$ responses.

A “do-nothing” module that refocuses all chemical shift evolutions and spin-spin splittings can be fashioned from the module which creates $e^{i\phi I_z}$ by choosing $8\tau \delta I$ to be an integral number of complete rotations, (as is essentially the case in Fig 3(a) and 3(e)). A general “do nothing” sequence, valid for any duration $8\tau$, can be constructed by introducing two hard (non-selective) $\pi$ pulses at times $4\tau$ and $8\tau$, where the trajectories of $I$, $R$ and $S$ are at a focus (Fig. 1).

2.2 Module O2: Selective rotation

The O1 phase evolution sequence (a rotation about the $z$ axis) can be converted into a module which produces rotation of a given spin by an arbitrary angle about an arbitrary axis (with no effect on the other spins). The principle of “decoupling” the rotation of the active ($I$) spins from the motion of the spectator spins ($R$ and $S$) was tested on the protons of 2,3-dibromopropanoic acid by imposing an $I$-spin rotation through $\phi = \pi$ radians about an axis in the $xz$ plane tilted at $\beta = \pi/4$ radians. This takes $+z$ magnetization to the $+x$ axis, for example. These experiments exploited an improved RE-BURP pulse (effective bandwidth 25 Hz), re-optimized to give more uniform re-focusing and better out-of-band suppression. Precautions were taken to compensate the effects of spin-lattice relaxation (which acts unequally during the different $\tau$ intervals) by increasing the tilt angle $\beta$ beyond $\pi/4$ radians. The experimental results (Fig. 4a) confirm the principle of decoupled rotation, showing a strong excitation of the $I$-spin response and residual responses from the spectators $R$ and $S$ reduced by more than an order of magnitude. Simulations were performed for this sequence based on numerical integration of the Liouville-von Neumann equation, neglecting relaxation but allowing for strong coupling. They indicate similar levels of residual responses for $R$ and $S$ (Fig. 4b).

2.3 Module O3: Selective evolution under the scalar coupling

The sequence shown in Fig. 2 implements the principal part of a CNOT gate, namely the unitary operator $e^{i\phi 2I_z S_z}$. Hard $\pi$ pulses are applied at times $2\tau$ and $6\tau$, where the $J_{IR}$
splittings of the $I$-spin response and the $J_{SR}$ splitting of the $S$-spin response are at a focus. In this experiment the preparation stage involved the excitation of $y$ magnetization. The $I$-spin and $S$-spin chemical shifts are refocused but the splitting $J_{IS}$ continues to generate diverging trajectories throughout the sequence, giving rise to a phase evolution of $\pm 8\pi J_{IS}$ radians on both the $I$-spin and $S$-spin responses. This is illustrated in Fig. 5 for phase increments of $\pm \pi/2$ radians. On traces (b) and (d) the (antiphase) $I$ and $S$ responses would have appeared in dispersion; for the sake of clarity the receiver phase was changed by $\pi/2$ to reset them to the absorption mode. The $R$ spin response remains essentially unchanged throughout.

3 “Much Ado About Nothing?”

Whereas classic NMR experiments commonly ignore collateral perturbation of coupled neighbour spins, a quantum computer requires that all these “spectator” spins return to their initial states at the end of the manipulation. For pulse sequences that are not instantaneous, this “do nothing” operation is by no means trivial; it necessitates exact refocusing of chemical shifts and spin-spin splittings.

We have demonstrated how selectivity can be achieved in a homonuclear coupled three-spin system for three important basic operations – phase evolution, an arbitrary rotation, and evolution under the scalar coupling. Note that these operations do not assume that the spin system is initially at Boltzmann equilibrium; the new “modules” are unitary operators that act on an arbitrary initial state of the spin system.

For NMR to be a useful technology for quantum computation, it will be necessary to extend current ideas to systems of many more spins. Indeed recent work suggests that only for such extended systems will the computations be fully quantum mechanical [16]. The extension of these soft pulse sequences to accommodate more spectator spins is straightforward, although in practice this lengthens the duration of the sequence. We must remember, however, that future implementations of NMR quantum computers need not be restricted to groups of coupled protons, so the selectivity requirements could be far less severe than in the present proton experiments, implying much shorter radiofrequency pulses.
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Figure Captions

Fig. 1. (Top) The O1 module. This sequence of soft π pulses (ellipses) is designed to allow phase evolution of the four I-spin magnetization components due to their chemical shift (dotted line) without spin-spin splittings, returning the coupled R and S spins to their initial states. (Bottom) Phase evolution diagram for the four I lines.

Fig. 2. (Top) The O3 module designed to focus the I, S and R chemical shifts but allow divergence of I and S magnetization components due to J_{IS}. Ellipses represent soft pulses. (Bottom) The phase evolution of the four I lines.

Fig. 3. Experimental test of the O1 module which allows phase evolution of transverse magnetization of the I spins without affecting the R and S responses. The quiet version of the soft π pulses was used (RE-BURP-Q) with a bandwidth of 40 Hz. The duration of the sequence (8τ) was incremented to give phase steps of π/2 radians over a range of 2π.

Fig. 4.(a) Experimental test of an O2 module which rotates the I magnetization through π radians about an axis tilted through π/4 radians in the xz plane, leaving the S and R spins largely unaffected. The RE-BURP-Q soft pulse had a bandwidth of 25 Hz and a duration of 220 ms. The soft pulse sequence of Fig. 1 was used, but with the assignment of soft pulses to S and R interchanged. In practice the tilt angle was made appreciably larger than π/4 to compensate for spin-lattice relaxation effects. (b) Simulated spectrum allowing for strong coupling but neglecting relaxation.

Fig. 5. Experimental test of the O3 module in which J_{IS} causes phase divergence of the I and S transverse magnetization spanning a range of ±2π radians in steps of ±π/2 radians. RE-BURP pulses with a 40 Hz bandwidth and a duration of 121 ms were used. In traces (b) and (d) the receiver phase was shifted by π/2 for the I and S responses in order to reset them to pure absorption.
Linden et al. Figure 1
Linden et al. Figure 2
Linden et al. Figure 3
