COMMUNICATIONS

High-Order Selective Sequences in Multiple-Quantum NMR

In a recent letter (1) we showed that multiple-quantum NMR transitions can be selectively excited, corresponding to the absorption of only groups of \(n\) photons. By a phase-shifted pulse sequence, a zero-order average Hamiltonian \(\mathcal{H}^{(0)}\) is produced which is \(nk\)-quantum selective, i.e., contains only matrix elements between states differing in energy by \(nk\hbar\omega_0\) \((k = 0, 1, 2, \ldots)\). In general, the propagator for any time-dependent sequence of pulses and delays may be written from average Hamiltonian theory (2) as \(U = \exp(-i\mathcal{H}(n_c, t_c))\), where \(t_c\) is the cycle time, \(n_c\) is the number of cycles, and \(\mathcal{H}\) is the effective time-independent Hamiltonian

\[
\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)} + \mathcal{H}^{(2)} + \cdots + \mathcal{H}^{(j)} + \cdots
\]

The quantity \(\mathcal{H}^{(0)}\) is the zero-order or average Hamiltonian; \(\mathcal{H}^{(j)}\) is termed a correction term of order \(j\), and is proportional to \((t_c)^j\). For \(t_c \rightarrow 0\), \(\mathcal{H}^{(0)}\) is the dominant term, and this is the term we made selective in our preliminary work which demonstrated 0, 4-quantum selectivity in oriented benzene.

A crucial aspect of this work, which allowed \(t_c \rightarrow 0\), was a time-reversible excitation \(\tilde{H}_p\) which produced, independent of the cycle time, an effective subcycle Hamiltonian \(\tilde{H}_0\) with all multiple-quantum components. In many systems (isotropic solutions, for example) \(t_c\) cannot be made vanishingly small while keeping multiple-quantum components in \(\tilde{H}_0\). In this case the terms \(\mathcal{H}^{(j)}\) for \(j \neq 0\), which are not necessarily selective, will contribute to \(\tilde{H}\) and ruin the selectivity. Thus a critical question is whether an excitation can be designed in the most general case such that the nonselective contributions to \(\mathcal{H}^{(j)}\) are reduced, making selective excitation generally applicable to spectroscopic systems and to large values of \(n\). In this communication we show for the first time the result that an excitation can be produced with an effective \(\tilde{H}\) which is \(nk\)-quantum selective for all terms \(\mathcal{H}^{(j)}\) up to arbitrarily high \(j\). This is done by a successive sequence of phase cyclings (described below) and can be used to produce highly \(nk\)-quantum selective excitation even when time reversal is not possible or when \(t_c\) cannot be made small enough to neglect correction terms.

We define a \(j\)-order \(nk\)-quantum selective sequence as one in which all terms \(\mathcal{H}^{(i)}\) \((i \leq j)\) in the average Hamiltonian expansion are \(nk\)-quantum selective, i.e., they are invariant to a rotation of \(\phi = 2\pi/n\) about the axis of quantization. These terms therefore can be decomposed into irreducible tensor operators \(T_{\mp p}^{(i)}\) with components \(p = nk\) \((k = 0, 1, 2, \ldots)\) and ranks \(l \geq |p|\). We define phase cycling, shown in Fig. 1a, as follows. We start with a sequence with an effective Hamiltonian \(\tilde{H} = \tilde{H}_0 = \mathcal{H}_0^{(0)} + \mathcal{H}_0^{(1)} + \cdots\), which is applied for a time \(\Delta \tau_p\), called a subcycle. The subcycle sequence is then repeated with the

\(^1\) Pure \(n\)-quantum selectivity \((k = 1)\) is also possible.
phase of all radiation shifted by $\phi = 2\pi/n$. This new sequence has an effective Hamiltonian $\tilde{H}_0$, which is related to $H_0$ by a rotation of $-\phi$ about the z axis, $\tilde{H}_0 = \exp(i\phi I_z)H_0 \exp(-i\phi I_z)$.

This phase shift is repeated $n$ times to form a cycle. The average Hamiltonian for the cycle is $\mathcal{H}^{(n)} = \sum_m \mathcal{H}^{(n)}_{m \pm n}$, which is $nk$-quantum selective even if $H_0$ is nonselective. If $H_0$ is already $j$-order selective, we can show that a similar expression holds for the nonselective part of $\mathcal{H}^{(n)}$, $j' \leq j + 1$. Therefore, if $H_0$ is $j$-order $nk$-quantum selective, the sequence obtained from $H_0$ by phase cycling is $(j + 1)$-order $nk$-quantum selective. Starting from any $H_0$, phase cycling increases the selectivity of the cycle to one order greater than the selectivity of the subcycles, while lengthening the sequence by factor of $n$. Using phase cycling alone, a $j$-order $nk$-quantum sequence $(k = 0, 1, 2, \ldots)$ can be designed from a nonselective sequence by $(j + 1)$ phase cyclings, requiring $n^{(j+1)}$ subcycles.

The number of subcycles needed can be reduced by the principle of symmetrization and the well-known fact (2) that all odd-order terms $\mathcal{H}^{(2j+1)}$ vanish for a symmetric sequence. Thus, the symmetrized sequence illustrated in Fig. 1b will raise the selectivity by two orders, if $H_0$ is already $(2j + 1)$-order selective, but this sequence requires only $2n$ subcycles instead of the $n^2$ subcycles required for two phase cyclings. Starting with a nonselective $H_0$, a $2j$-order selective sequence requires $n(2n)^j$ subcycles ($(j + 1)$ phase cyclings and/or symmetrizations) and a $(2j + 1)$-order sequence requires $(2n)^{j+1}$ subcycles ($(j + 1)$

\(^2\) Other permutations of the $n$ values of $\phi$ are also acceptable and may be advantageous in many cases.
phase cyclings and \((j+1)\) symmetrizations). For example, a third-order \(4k\)-quantum selective sequence requires 64 subcycles (two phase cycles and two symmetrizations) and can be written schematically \((0: \phi = 0, 1: \phi = \pi/2, 2: \phi = \pi, 3: \phi = 3\pi/2)\) as

\[
\begin{align*}
(01233210) & (12300321) (23011032) (30122103) \\
(30122103) & (23011032) (12300321) (01233210).
\end{align*}
\]

In our previous work we incorporated time reversal in the sequence for \(\hat{H}_0\) shown in Fig. 1c. The quantity \(\hat{H}_p\) appears as a unitary transformation on \(H_{zz}\), so that \(\hat{H}_0\) can contain multiple-quantum coherence if \(\|H_0T\| \gg 1\). However, \(\|\mathcal{K}_0^{(0)} \Delta \tau_p\| = \|H_{zz} \Delta \tau'_p\|\), so \(\|\mathcal{K}_0^{(0)} \Delta \tau_p\|\) can be made arbitrarily small by reducing the ratio \(\Delta \tau'_p/\Delta \tau_p\). In this case, even a zero-order selective sequence will be effective. If time reversal is impossible, \(\hat{H}_0\) will not contain multiple-quantum coherences unless \(\|\hat{H}_0 \Delta \tau_p\| \geq 1\), and a zero-order selective sequence is useless. However, if a high-order selective sequence is used \(\|\hat{H}_0 \Delta \tau_p\|\) need not be small, and time reversal is not necessary for selectivity. We expect that a combination of high-order selectivity and time reversal, when possible, will give the best results. Applications of these sequences to selective excitation in multiple-quantum NMR will be described in a full paper, together with a quantitative treatment of selectivity.

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