Journal of Magnetic Resonance 248 (2014) 146–152

Contents lists available at ScienceDirect

Journal of Magnetic Resonance

journal homepage: www.elsevier.com/locate/jmr

Further perspective on the theory of heteronuclear decoupling

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ARTICLE INFO

Article history:
Received 10 April 2014
Revised 2 June 2014
Available online 24 June 2014

Keywords:
Decoupling theory
Broadband decoupling
Heteronuclear decoupling
IS spin system
J coupling
Optimal control theory

ABSTRACT

An exact general theory of heteronuclear decoupling is presented for spin-1/2 IS systems. RF irradiation applied to the *I* spins both modifies and generates additional couplings between states of the system. The recently derived equivalence between the dynamics of any *N*-level quantum system and a system of classical coupled harmonic oscillators makes explicit the exact physical couplings between states. Decoupling is thus more properly viewed as a complex intercoupling. The sign of antiphase magnetization plays a fundamental role in decoupling. A one-to-one correspondence is demonstrated between $\pm 2S_yI_z$ and the sense of the S-spin coupling evolution. Magnetization S_x is refocused to obtain the desired decoupled state when $\int 2S_yI_z\,dt = 0$. The exact instantaneous coupling at any time during the decoupling sequence is readily obtained in terms of the system states, showing that the creation of two-spin coherence is crucial for reducing the effective scalar coupling, as required for refocusing to occur. Representative examples from new aperiodic sequences as well as standard cyclic, periodic composite-pulse and adiabatic decoupling sequences illustrate the decoupling mechanism. The more general aperiodic sequences, obtained using optimal control, realize the potential inherent in the theory for significantly improved decoupling.

1. Introduction

The dominant strategy for designing broadband heteronuclear decoupling sequences for the past 30 years derives from average Hamiltonian theory [1,2]. If RF irradiation is applied to the *I* spins in a weakly coupled spin-$\frac{1}{2}$ IS system, effective decoupling of the *S* spins can be shown to occur if the *I* spins are cyclically returned to their initial state. The range of chemical shift offsets over which this is possible defines the bandwidth of the decoupling sequence.

At the same time, Waugh's theory of decoupling [3] showed that the cyclic condition is not crucial. The magnitude of the net rotation that a free (uncoupled) *I*-spin would undergo during a decoupling period only has to vary sufficiently slowly over the bandwidth. The variation of this net rotation with offset is small enough if it is approximately constant over frequency ranges equal to the scalar coupling. A net rotation of zero over the entire bandwidth, as required for cyclicity, is unnecessarily restrictive.

However, as emphasized in [3], the theory provides no insight or procedure for designing effective non-cyclic sequences. In addition, the theory has its own restrictions. Periodic irradiating sequences are assumed in the analysis, with one sampling point per period. Ideal decoupling is obtained if the in-phase magnetization at each sample is equal to its initial value (nominally, one). Deviations from this ideal represent modulations of the signal that appear as satellite lines or sidebands. Smaller deviations result in smaller sidebands. Sampling faster than the assumed rate, as in practical decoupling applications, was not considered critical, since it merely makes the sidebands more prominent. These restrictive assumptions were therefore justified on qualitative grounds, while recognizing their potential limitations with regard to effective decoupling. A more general theory for deriving good decoupling schemes was posed as a challenge for further consideration.

Thus, for lack of a better alternative, decoupling strategies have emphasized cyclic sequences. The standard approach is to find the best inversion pulse based on a set of desired criteria (power, bandwidth, etc.) and apply phase cycles to approach an ideally cyclic sequence [4–23]. A noteworthy example is the adoption of adiabatic pulses for the inversion element of the decoupling sequence [5,12–15], resulting in broadband inversion at lower power than composite pulses. There are a multitude of adiabatic pulses that can provide the necessary bandwidth for high-field spectroscopy at a given average pulse power level. They differ in the intensity of sidebands produced over the decoupled bandwidth [24]. Performance limits for ideal adiabatic decoupling have been derived that provide a standard for decoupling performance [25], but are themselves limited by the framework of cyclic decoupling strategies.

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http://dx.doi.org/10.1016/j.jmr.2014.06.002
1090-7807/

The present work shifts perspective from the irradiated I spins that are the focus in previous analyses of decoupling to the S spins. This immediately provides a unifying mechanism for decoupling, with no assumptions about the sequence itself. An exact, time-dependent coupling then emerges as a logical consequence of the decoupling mechanism. These results clarify possibilities for improved decoupling, unconstrained by the demands of periodic and cyclic sequences. Optimal control is able to realize this potential and, in effect, invert the theory to derive more effective decoupling schemes [26,27]. The fidelity of the derived decoupling mechanism is illustrated using both standard cyclic sequences and this new generation of improved, aperiodic decoupling sequences.

2. Theory

A brief summary of the existing theory of heteronuclear decoupling is provided to establish the context of standard cyclic decoupling strategies. This is followed by a new perspective on decoupling that is more general than Waugh's original treatment and delineates the mechanics underlying decoupled IS systems.

2.1. The decoupled signal

The Liouville–von Neumann equation for the time evolution of a density matrix ρ governed by system Hamiltonian $\mathcal{H}$ is

$$\dot{\rho} = -i[\mathcal{H}, \rho]. \quad (1)$$

For time-independent $\mathcal{H}$, the formal solution is

$$\rho(t) = e^{-iHt}\rho(0)\,e^{iHt} = U\rho(0)U^{\dagger}, \quad (2)$$

which defines the propagator $U(t) = e^{-iHt}$.

Constant RF irradiation of amplitude $\omega_{\rm rf}$ and phase ϕ, or, (x, y) components (ω_1, ω_2), and offset ω_3 relative to the resonance frequency of the I spins results in an effective field in the rotating frame of the I spins written (in angular frequency units) as

$$\boldsymbol{\omega}_e = \omega_{\rm rf}[\cos\phi\,\hat{\boldsymbol{x}} + \sin\phi\,\hat{\boldsymbol{y}}] + \omega_3\,\hat{\boldsymbol{z}} = \omega_1\,\hat{\boldsymbol{x}} + \omega_2\,\hat{\boldsymbol{y}} + \omega_3\,\hat{\boldsymbol{z}}. \quad (3)$$

In the weak coupling limit, the Hamiltonian for on-resonance S spins is

$$\mathcal{H} = \boldsymbol{\omega}_e \cdot \boldsymbol{I} + \mathcal{J} S_z I_z, \quad (4)$$

where $\mathcal{J}$ is 2π times the coupling J in Hertz. $\mathcal{H}$ can be described in terms of equivalent effective fields $\boldsymbol{\omega}_{\pm} = \boldsymbol{\omega}_e \pm \mathcal{J}/2\,\hat{\boldsymbol{z}}$, giving a propagator comprised of $U_{\pm}(t) = e^{-i(\boldsymbol{\omega}_{\pm}\cdot\boldsymbol{I})t}$ [3].

Since $[S_z, \mathcal{H}] = 0$, the offset effect of spin S can be calculated separately. It is therefore sufficient to consider the S spins on resonance, with solution [3]

$$S_x(t) = \frac{(1 + \hat{\boldsymbol{\omega}}_{+}\cdot\hat{\boldsymbol{\omega}}_{-})}{2}\cos\frac{(\omega_{+}t - \omega_{-}t)}{2} + \frac{(1 - \hat{\boldsymbol{\omega}}_{+}\cdot\hat{\boldsymbol{\omega}}_{-})}{2}\cos\frac{(\omega_{+}t + \omega_{-}t)}{2}, \quad (5)$$

where $\hat{\boldsymbol{\omega}}_{\pm}$ are unit vectors in the direction of the equivalent effective fields.

2.2. Standard decoupling strategy: an I spin emphasis

Eq. (5) forms the basis for an interpretation of decoupling in terms of I spin evolution [3], summarized here as follows. A shaped RF pulse is typically applied in discrete steps of length Δt at successive times $t_k = k\Delta t$ during which the amplitude $\omega_{\rm rf}^{(k)}$ and phase $\phi^{(k)}$ are constant. Each propagator $U_{\pm}^{(k)}$, if operating on an uncoupled I spin during interval k, would generate a rotation about respective axes $\hat{\boldsymbol{\omega}}_{\pm}^{(k)}$ by angles $\beta_{\pm}^{(k)} = \omega_{\pm}^{(k)}\Delta t$. At time t_n, the $U_{\pm}(t_n)$ are the concatenation of the successive propagators $U_{\pm}^{(k)}$ $(k = 1, \ldots, n)$. The solution for $S_x(t_n)$ is then of the form given in Eq. (5), with $\omega_{\pm}t_n = \beta_{\pm}$ denoting equivalent net rotation angles about axes $\hat{\boldsymbol{\omega}}_{\pm}$, which can be determined after expanding the exponential in $U_{\pm}(t_n)$ to obtain

$$U_{\pm}(t_n) = \cos\left(\frac{1}{2}\beta_{\pm}\right) - i(\hat{\boldsymbol{\omega}}_{\pm}\cdot\boldsymbol{I})\sin\left(\frac{1}{2}\beta_{\pm}\right). \quad (6)$$

As noted in [3], if the sequence is cyclic at time t_n in the sense that $\beta_{\pm} \approx 0$, then $\hat{\boldsymbol{\omega}}_{+} \approx \hat{\boldsymbol{\omega}}_{-}$ and $S_x(t_n) = 1$. There is therefore no net coupling evolution, and S appears to be decoupled from the I spins. The second term in Eq. (5) is small under these conditions, responsible for the production of sidebands, and was generally ignored. Since the offset for each $\omega_{\pm}^{(k)}$ is equal to $\omega_3 \pm \mathcal{J}/2$, an equivalent interpretation is that the propagator for a free, uncoupled I spin ($\mathcal{J} = 0$ in Eq. (4)) should return the I spins to their initial state, independent of offset. Then $\beta_{\pm}$ is automatically zero over the given range of offsets, which defines the bandwidth for good decoupling.

This is the standard approach to developing good broadband decoupling sequences, proposed, prior to Waugh's analysis, by Levitt and Freeman [28] using average Hamiltonian theory. Other options for achieving $S_x(t_n) = 1$ do not lend themselves to such an intuitive picture. One possibility emphasized in [3] for periodic, but not necessarily cyclic, sequences is $\beta_{+} \approx \beta_{-}$ for rotation axes $\hat{\boldsymbol{\omega}}_{+} \approx \hat{\boldsymbol{\omega}}_{-}$. This is equivalent to requiring that the net rotation of a free I spin during a given t_n be relatively insensitive to offset over the range of the scalar coupling. Although this is more general than the cyclic criterion of net zero rotation, it is less clear how to achieve it.

There are other possibilities, as well, that justify sampling at times $t \le t_n$ and do not require periodicity in the sequence. If $\hat{\boldsymbol{\omega}}_{+}$ and $\hat{\boldsymbol{\omega}}_{-}$ are nearly perpendicular, then for sufficiently small (but not necessarily equal) $\beta_{\pm} = \omega_{\pm}t$, the cosine terms in Eq. (5) are each approximately equal to one, giving $S_x(t) \approx 1$. Solutions satisfying this set of conditions can be found, ironically, in decoupling sequences designed according to the cyclic standard $\beta_{\pm} = 0$, underscoring Waugh's insight that good decoupling does not require cyclicity. In addition, they also highlight the significance of the second term in Eq. (5), which most generally is not small relative to the first term.

There are, in principle, innumerable combinations of $\hat{\boldsymbol{\omega}}_{\pm}$ and $\beta_{\pm}$ that give a solution $S_x(t) \approx 1$. Further detail is provided in Section 3. A more general approach to decoupling than either the cyclic or periodic standard might determine some number of these combinations and set about devising I spin propagators to access them. If this is not difficult enough, one should also be able to distinguish between the relative merits of various combinations (most of which remain unknown) as the propagator is being derived. One immediately understands and appreciates the exclusive focus on cyclic decoupling methods during the 30 years since Waugh suggested there should be other possibilities.

Shifting focus to the S spins and evolution of the states given by the complete solution for $\rho(t)$ [29–31] provides a more fruitful approach for understanding and developing improved decoupling sequences.

2.3. New perspective on decoupling: an S spin emphasis

Initial $\rho(0) = S_x$ also evolves to states $2S_yI_j$, $(j = 1, 2, 3 \equiv x, y, z)$ which, although not directly detectable, are important for understanding the mechanism of decoupling. The Hamiltonian of Eq. (4), in fact, restricts the time evolution of operators in the set $\{S_x, 2S_yI_j\}$ to the subspace spanned by these same operators, and similarly for the set $\{S_y, 2S_xI_j\}$ [29], as can be seen by calculating the commutator in Eq. (1). Complete solutions for the evolution of any state in either closed set to the other states in the respective set are given in [29–31]. Defining $S_{+} = S_x + iS_y$ and writing the