Journal of the Korean Magnetic Resonance Society **1999**, *3*, 36-43

Computer-Aided Crafting of Pulse Shapes for Broadband Heteronuclear Decoupling in the presence of Homonuclear Coupling

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Received May 7, 1999

Abstract: We present a pulse shape tailored for broadband decoupling for a system of spin-1/2's with scalar couplings as well. In crafting the pulse shape Coherent Averaging Theory and Fourier expansion method are used. The Fourier expansion coefficients are optimized numerically by applying the Simulated Annealing Method. The decoupling performance of the shaped pulse thus designed is then compared with the well-known composite pulse sequence, DIPSI-2. It is shown that the shaped pulse performs well even at the conditions where the DIPSI sequence begins to fail.

INTRODUCTION

The use of shaped pulses in magnetic resonance and coherent spectroscopy in optical domain has been quite successful in overcoming the limitations that arise from the use of rectangular pulses and various novel pulse shape effects have been discovered.[1] For a two-state system, such as an isolated spin-1/2 or a two-level atom, there exist systematic techniques for finding a desired shape by inverting the Bloch equation.[2] Such inversion techniques are based on the methods of one-dimensional inverse scattering transform(IST) method on the entire real axis.[3] For example, exact analytical shapes of a family of $2N\pi$ (N=1,2,3,...) pulses [4] and of a $\pi/2$ pulse [5] have been found using IST. For the latter case, it is equally legitimate to cast the problem into one on the positive real axis (*i.e.* a radial problem), yielding an identical solution.[6]

The above pulses are expressly for a single two-state system. If there are more than two states involved in the dynamics, there are no known techniques for obtaining exact analytical pulse shapes and the next best thing one has is to resort to approximate methods. An example of multi-state problem in magnetic resonance is the decoupling of C-H in the presence of H-H couplings. For this case, there is a well-known family of composite pulse sequences, DIPSI-*n*.[7] The purpose of this paper is to find pulse shapes for that problem and compare their decoupling performance with that of DIPSI-2, the most practical one in the aforementioned family.

THEORY

Coherent Averaging Theory

The time development of a spin system is governed by the evolution operator

$$U(t,0) = \overleftarrow{\tau} \exp\left(-\frac{i}{\hbar}\int_0^t H(t')dt'\right), \tag{1}$$

where $H(t)$ is the Hamiltonian, the time dependence originating from applied pulses, and $\overleftarrow{\tau}$ is the time-ordering operator. For most problems direct evaluation of (1) is not possible. In case of cyclic perturbations, observations may be made stroboscopically once for each cycle time t_c and the evolution operator may be expressed in terms of an effective average Hamilotonian during a cycle $\overline{H}$ such that

$$U(t = Ntc) = \exp\left(-\frac{i}{\hbar}\overline{H}Ntc\right) = \exp\left(-\frac{i}{\hbar}\overline{H}tc\right) \tag{2}$$

Consequently, it suffices to find $\overline{H}$. (We set $\hbar = 1$ in subsequent discussions, for simplicity.) In practice, the effective Hamiltonian is approximated by the Magnus expansion:[8]

$$\overline{H}tc = \sum_{K=0}^{\infty} \overline{H}^{(K)}(tc) \ , \tag{3}$$

where the first two terms are

$$i\overline{H}^{(0)} = \frac{i}{tc}\int_0^{tc} \widetilde{H}(t')dt' \tag{4}$$

and

$$i\overline{H}^{(1)} = \frac{i^2}{2!tc}\int_0^{t_c}\int_0^{t_1} [\widetilde{H}(t_1), \widetilde{H}(t_2)]dt_1dt_2 \tag{5}$$

In the above $\tilde{H}(t) \equiv U_{rf}(t)^{\dagger} H U_{rf}(t)$ is the switched internal Hamiltonian produced by the R. F. pulse. Equations (2)-(5) constitute the Coherent Averaging Theory.[9]

Effective Hamiltonian for the coupled spins

Now consider the coupled spin system. In general, we are concerned with a system consisting of an arbitrary number of C-13 nuclei coupled to an arbitrary number of H's, the H spins being also coupled with each other. Modeling such a general system is next to an impossibility, so we will consider a much simplified system consisting of two H nuclei and a C-13. In this system there is a H-H coupling as well as a C-H coupling, so the most important features of the general system are expected to emerge from the study of this system.

The Hamiltonian for the system is conveniently expressed by assuming, without loss of generality, that the decoupler is set on resonance with the first proton resonance frequency:

$$H = \Delta\omega I_z + J\,\mathbf{I}_1 \cdot \mathbf{I}_2 + \omega_2 I_x \tag{6}$$

In the above $\Delta\omega$, J, and ω_2 are the second-H spin resonance offset, H-H coupling constant, and decoupler amplitude, respectively. The C-H coupling term is in effect a single-spin operator term that behaves the same as the offset term, so it has been absorbed in $\Delta\omega$.

The zeroth-order Hamiltonian for this system is given by

$$\overline{H}^{(0)} = \frac{\Delta\omega}{tp} \int_0^{t_p} \left[I_{2z} \cos\theta(t) + I_{2y} \sin\theta(t) \right] dt + J\,\mathbf{I}_1 \cdot \mathbf{I}_2 \quad , \tag{7}$$

where t_p is the pulse width and

$$\theta(t) = \int_0^t \omega_2(t')dt' \tag{8}$$

is the pulse flip angle. Higher-order terms in the Magnus expansion may similarly be expressed.

Numerical optimization

For heteronuclear decoupling one has to remove all offset-dependent terms from these Hamiltonian terms-an onorous task. In this paper we attempt to remove the offset term in the zeroth order Hamiltonian. Thus, the goal function to minimize is

$$G(\{a_n\}) = \left| \int_0^{t_p} \cos\theta(t)dt \right| + \left| \int_0^{t_p} \sin\theta(t)dt \right| , \tag{9}$$

where $\{ a_n \}$ denotes a set of parameters to vary and optimize.

If we wish to obtain the pulse shape numerically, it may be parameterized quite generally as a Fourier sum

$$\omega_2(t) = a_0 + \sum_{n=1}^{m} a_n \cos n\omega t + \sum_{n=1}^{m'} b_n \sin n\omega t , \tag{10}$$

where the coefficients are to be optimized and $m(m')$ denotes the number of coefficients to be optimized. It is well known that for decoupling purposes π pulses are better than π/2 pulses, so we optimize the coefficients subject to the constraint $\theta\ t_p = \pi$ and we also set $\omega = 1/t_p$. For simplicity, we only use cosine terms in this paper.

There are several optimization routines. However, most routines find *local* minima, which may not make the goal function vanish. The best known method for finding the *global* minimum is the simulated annealing method.[10] It is described well in the literature,[11] so we will not go into details of the implementation of the method. As a moderate

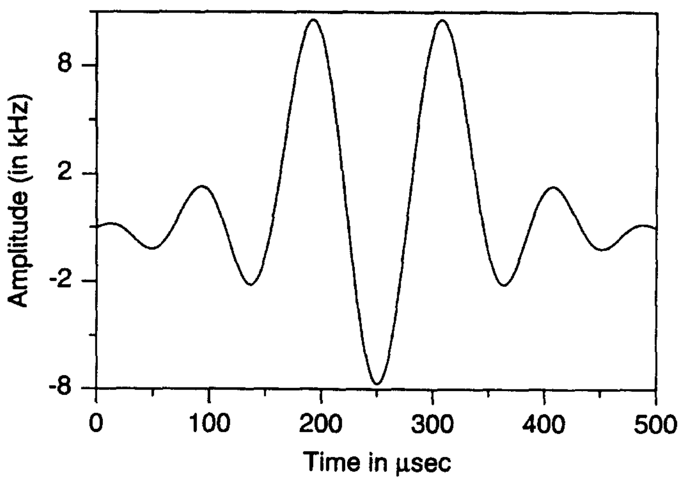

Fig. 1. Shape of the pulse. The amplitude is in units of kHz and time is in μsec. The rms amplitude of the pulse is 3.993 KHz.

size optimization we tried with six cosine terms. A result of the simulated annealing method for the offset-independent π pulse is

$$a_1 = 1.39,\ a_2 = -0.45,\ a_3 = -2.17,\ a_4 = -3.39,\ a_5 = -4.23,\ a_6 = 0.50. \tag{11}$$

In the above all coefficients are in units of kHz. Of course, it is always possible, at the expense of more computer time, to increase the number of coefficients to make the bandwidth appreciably larger. The shape of the pulse is shown in Fig. 1. The root-mean-square amplitude with $t_p = 500$ μsec is 3.993 kHz.

Evaluation of pulse performance

To evaluate the decoupling performance of the shaped pulse we consider the spin system with the following coupling constants:

$$\Delta\omega_1 = 2000,\ \Delta\omega_2 = -1500,\ J_{H\text{-}H} = 15,\ J_{C\text{-}H,1} = 150,\ J_{C\text{-}H,2} = 0\ \text{(all in units of Hz)}\ . \tag{12}$$

We compared the decoupling performance of a usual rectangular pulse, the composite pulse DIPSI-2, and the above shaped pulse with a similar pulse strength (4 kHz amplitude for the rectangular pulse and DIPSI-2, and 3.993 kHz rms amplitude for the shaped pulse). The rectangular and shaped π pulses are applied repeatedly. On the other hand, for DIPSI-2 (here denoted as R) the sequence $R\bar{R}\bar{R}R$ is used, as recommended in the literature.[7] This makes the DIPSI sequence quite long as compared with the shaped pulse.

The simulated H spectra under the three decoupling pulse types for the aforementioned system are compared in Fig. 2. If the decoupling is perfect, one will get an isotropic Hamiltonian, $H = J\,\mathbf{I}\cdot\mathbf{I}$ and the spectrum will show a single peak at the center. For these spectra 0.2 Hz of line broadening is given. As expected, the DIPSI-2 sequence and the shaped pulse improve upon the performance of the rectangular pulse substantially. Note, however, that the performance of even a single (as opposed to a sequence) shaped pulse is more robust than that of DIPSI-2, which just begins to fail at the particular set of parameters of the Hamiltonian.

CONCLUSION

Broadband pulses designed for two-level systems, such as WALTZ-16[12] and hyperbolic secant shaped pulse,[13] cannot be applied to multilevel systems. Then one has to settle for approximation in designing either composite pulses or shaped pulses using, for example, the Coherent Averaging Theory. We have shown that a rudimentary shaped pulse, if well designed, can outperform the best composite pulse. As one incorporates more higher terms in the Magnus expansion, one gets pulses that perform better, although the goal function to optimize will be much more complicated. Here, if the number of levels is *N*, the *SU*(*N*)-Lie algebraic relations should find much utility.[14] However, there is an additional way to simplify the problem based on the symmetry property of the Magnus expansion: if a pulse sequence is antisymmetric in time, it is known that *all odd-order terms vanish identically*.[15]

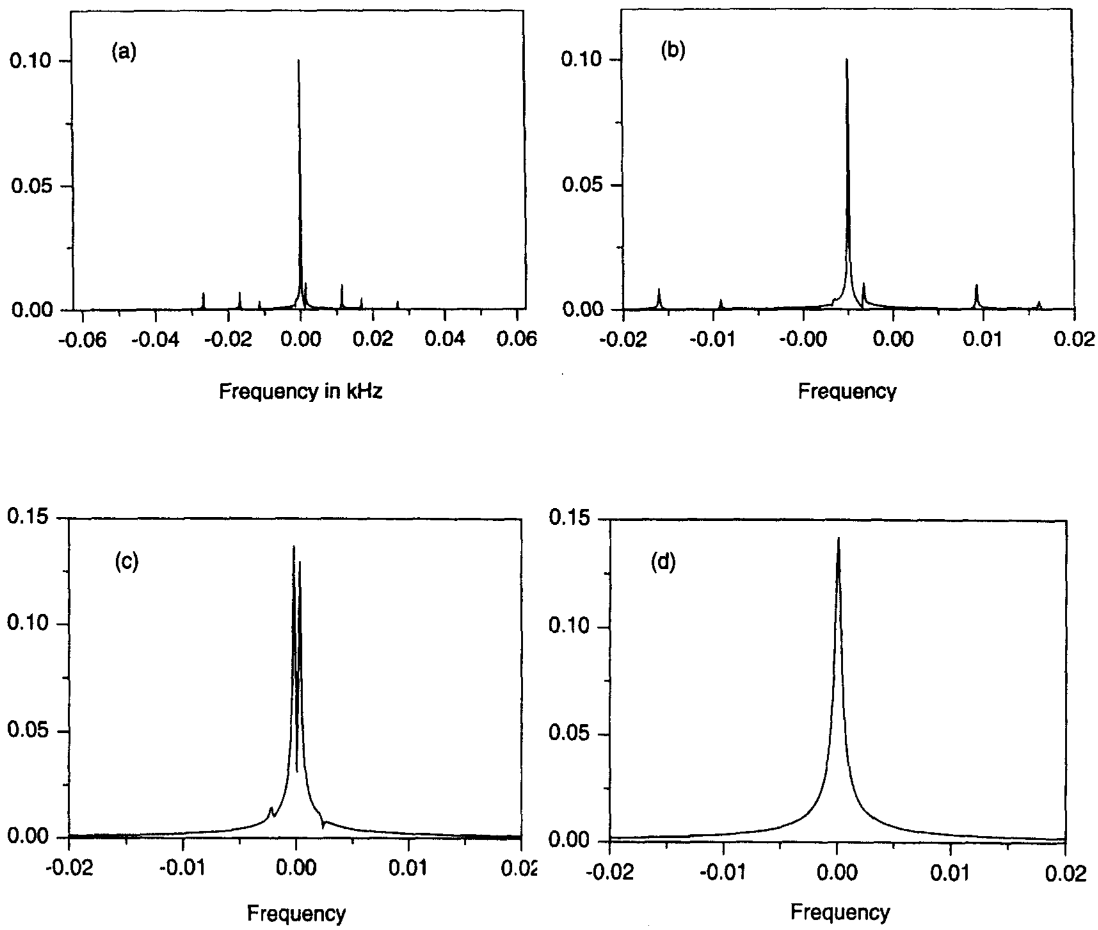

Fig. 2. H spectra under decoupling pulses : (a) rectangular pulse. (b) detailed view of the spectrum under the rectangular pulse. (c) DIPSI-2. (d) shaped pulse.

Therefore, by designing the sequence antisymmetric, one does not have to worry about the first, the third,... terms. It is not difficult to modify our design approach to take advantage of the symmetry property of the Magnus expansion. Progress in broadband decoupling is important. The creation of isotropic Hamiltonian can serve as a mixing Hamiltonian in coherence (or magnetization) transfer experiments.[16]

Acknowledgements

This work was supported by the '97 Institutional Research Fund of Sunmoon University.

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