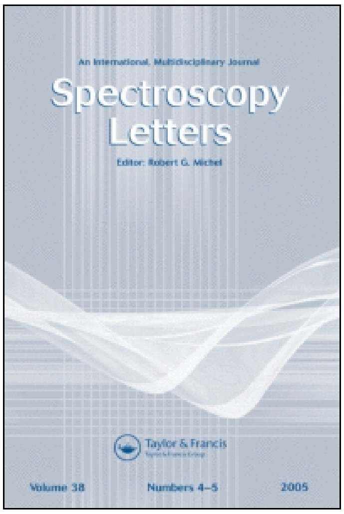

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Composite Pulse NMR with Phase Distortion

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ABSTRACT

A phase-distorting composite pulse NMR method is described. In the calculation, it only uses function Z22, representing the Wigner rotation matrix elements. The optimum composite pulse sequence parameters were obtained by minimizing the pulse angles and phase distortion effects, this new route could greatly save computing time and efforts. Moreover, the experimental data are consistent with the theoretical results, and it is compared with other existing compostite pulse sequences.

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INTRODUCTION

Computer has been widely used in designing NMR multipole pulse sequences of one- and two-dimensional spectroscopy, in which composite pulses have proved the usefulness in spin echo experiments[1], broadband decoupling sequences[2], homonuclear TOCSY (Total Correlation Spectroscopy)[3], description of two-dimensional NMR experiment[4], Hetero-Tocsy experiment with RF mixing pulse sequences[5], as well as assignment of the two-dimensional ^{1}H NMR spectra[6].

Previously, we have reported a phase-alternating composite pulse method[7], in which the composite pulses could rotate magnetization from its equilibrium position paralleled to the static magnetic field (H_0). These rotations were described by the Wigner rotation matrices. It was demonstrated that a phase-alternating composite pulses could give a clear physical picture, the transformation of which involved the change of rotation axis ($\varphi_{i+1}=\varphi_i+\pi, i=1,\cdots,n$, set $\varphi_1=0$) while keeping the rotation fixed. However, for composite π pulses with phase distortion (phase-unalternated), the rotation matrices can be explicitly evaluated in trems of sins and cosines which allow the minimization of both flip angles and phase-distortion effects with respect to resonance offset ($\Delta\omega/\omega_1$). Therefore, the Wigner rotation matrices become very complicated. In addition, the first derivatives of the function are acted not only to flip angles, but to phase angles as well (any flip angles and phase angles).

A composite pulse with N components is described by 2N parameters, being flip angle β and phase angle φ of each component pulse, can be written as a 2N dimensional vector $x\equiv(\beta_1,\cdots,\beta_n,\varphi_1,\cdots,\varphi_n)$. The overall efficiency of a composite pulse can be characterised by function F(x), defined as[8]

$$F(x)=\sum_{i=1}^{M} f_i(x,d_i)^2 \quad x\equiv(\beta_1,\cdots,\beta_n,\varphi_1,\cdots,\varphi_n) \qquad (1)$$

Where $M \geqslant N$, d_i represents points of resonance offset $(\Delta\omega_i/\omega_{1i})$, called DEL. Minimizing $F(x)$ with respect to the parameters $\beta_i, \varphi_i (i = 1, \cdots, n)$ and resonance offset $(\Delta\omega/\omega_1)$ will yield the optimum composite pulse parameters. This minimization can be achieved by altering the resonance offset $(\Delta\omega/\omega_1)$, flip and phase angles, until the "better-result" is obtained.

THEORY AND CALCULATIONS

For a phase-distortion, the treatment of compostite π pulses can be defined in terms of products of the rotations. In the multipole bases, these rotations are represented by the Wigner rotation matrices, the elements of Wigner rotation matrix $\mathscr{D}^{(K)}_{qq'}(\Omega_{1\cdots n})$ are given as follows[9]

$$\begin{aligned}\mathscr{D}^{(K)}_{qq'}(\Omega_{1\cdots n}) = \sum_{\text{all}q'} & \exp(iq(\alpha_1 - \varphi_1 + \pi))d^{(K)}_{qq_1}(\beta_1) \\ & \cdot \exp(iq_1(\alpha_1 + \alpha_2 + \varphi_1 - \varphi_2 + \pi))d^{(K)}_{q_1q_2}(\beta_2) \\ & \cdot \exp(iq_2(\alpha_2 + \alpha_3 + \varphi_2 - \varphi_3 + \pi))\cdots \\ & \cdot d^{(K)}_{q_{n-1}q'}(\beta_n)\exp(iq'(\alpha_n + \varphi_n)) \qquad (2)\end{aligned}$$

where K is the tensor rank, q the spherical component, and Ω the Euler angle which may be shown as

$$\Omega = (\alpha + \varphi, \beta, \alpha - \varphi + \Delta\omega t + \pi)$$

where α is the azimuthal angle, β the flip angle, and the phase of the pulse is φ. The Wigner rotation matrix elements depend on the variable α, β and φ, and they also rely on radio frequency and resonance offset. These parameters are defined as

$$\omega_1 = \gamma H_1 \qquad \omega_0 = \gamma H_0$$

$$\Delta\omega = \omega - \omega_0 \qquad \Omega = \sqrt{\Delta\omega^2 + \omega_1^2}$$

where ω_1 is the radio frequency amplitude, ω_0 the Larmor frequency, ω the frame rotation frequency, and Ω the resonance offset frequency. The azimuthal angle α and the flip angle β appeared in the Wigner rotation matrices can be shown as follows

$$\sin(\alpha) = -\cos\left[\frac{\Omega t}{2}\right]\left[1 - \frac{\omega_1^2}{\Omega^2}\sin^2\left[\frac{\Omega t}{2}\right]\right]^{-\frac{1}{2}}$$

$$\cos(\alpha)=-\frac{\Delta\omega}{\Omega}\sin\left[\frac{\Omega t}{2}\right]\left[1-\frac{\omega_1^2}{\Omega^2}\sin^2\left[\frac{\Omega t}{2}\right]\right]^{-\frac{1}{2}}$$

$$\sin(\beta)=\frac{2\omega_1}{\Omega}\sin\left[\frac{\Omega t}{2}\right]\left[1-\frac{\omega_1^2}{\Omega^2}\sin^2\left[\frac{\Omega t}{2}\right]\right]^{\frac{1}{2}}$$

$$\cos(\beta)=\frac{1}{\Omega^2}[\Delta\omega^2+\omega_1^2\cos(\Omega t)]$$

For systems of isolated spin-$\frac{1}{2}$ nuclei or systems of high spin I, only elements of the rotation matrix $\mathscr{D}^{(1)}_{qq'}$ need to be considered, with making use of the generating function for the reduced matrix element $d^{(K)}_{m'm}(\beta)$ as given by Edmonds[10]. An n-composite π pulse with phase-distortion can be expressed as products of 3×3 matrix, called Z matrix, and the matrix element Z22 is a function of α, β and φ, are given in reference[9]

$$\begin{aligned}Z22 &= \cos(\beta_{1\cdots n})\\ &= \cos(\beta_{1\cdots n-1})\cos(\beta_n)-A_{1\cdots n-1}\sin(\beta_n)\cos(\alpha_{n-1}\\ &\quad+\alpha_n+\varphi_{n-1}-\varphi_n+\pi)+\beta_{1\cdots n-1}\sin(\beta_n)\sin(\alpha_{n-1}\\ &\quad+\alpha_n+\varphi_{n-1}-\varphi_n+\pi)\end{aligned} \tag{3}$$

where

$$\begin{aligned}A_{1\cdots n}&=\cos(\beta_{1\cdots n-1})\sin(\beta_n)+\sin(\beta_{1\cdots n-1})\\ &\quad\bullet\cos(\beta_n)\cos(\alpha_{1\cdots n-1}+\alpha_n-\varphi_n+\pi)\\ B_{1\cdots n}&=\sin(\beta_{1\cdots n-1})\sin(\alpha_{1\cdots n-1}+\alpha_n-\varphi_n+\pi)\end{aligned} \tag{4}$$

The expressions given by equation (2) and (3) permit the generation of results of any composite pulse sequences in terms of dependent variable parameters $\Delta\omega$, ω_{1i} and φ_i, $i=1,\cdots,n$. Applying a π pulse on resonance, $\alpha=-\pi/2$, $\beta=\omega_1 t$, will rotate the magnetization from Z axis to $-$Z axis diraction

$$M_Z(t)=Z22(1)=\cos(\beta_1)=-1 \tag{5}$$

For an overall rotation of the case $n=2$, composite π pulse sequences are established simply from equation(3) and given by

$$\begin{aligned}Z22(2)&=\cos(\beta_{12})=\cos(\beta_1)\cos(\beta_2)-\sin(\beta_1)\sin(\beta_2)\\ &\quad\bullet\cos(\alpha_1+\alpha_2+\varphi_1-\varphi_2+\pi)\end{aligned} \tag{6}$$

For $n=3$, the Wigner rotation matrix element Z22 can be written as

$$Z22(3)=\cos(\beta_{123})=\cos(\beta_1)\cos(\beta_2)\cos(\beta_3)$$

$$-\sin(\beta_1)\sin(\beta_2)\sin(\beta_3)\cos(\alpha_1+\alpha_2+\varphi_1-\varphi_2+\pi)$$
$$-\sin(\beta_2)\sin(\beta_3)\cos(\beta_1)\cos(\alpha_2+\alpha_3+\varphi_2-\varphi_3+\pi)$$
$$-\sin(\beta_1)\sin(\beta_3)\cos(\beta_2)\cos(\alpha_1+\alpha_2-\varphi_2+\pi)$$
$$\cdot\cos(\alpha_2+\alpha_3+\varphi_2-\varphi_3+\pi)+\sin(\beta_1)\sin(\beta_3)\sin(\alpha_1$$
$$+\alpha_2-\varphi_2+\pi)\cdot\sin(\alpha_2+\alpha_3+\varphi_2-\varphi_3+\pi) \qquad (7)$$

It is obvious that the expression becomes substantially complicated as n is increased from 2 to 3.

The composite pulses with phase-distortion effects could be constructed by solving equation (2) either analytically or numerically. Function Z22 and its first derivatives (flip angles and phase angles) are required, which are calculated by using the algebraic computer language REDUCE

$$ZD122=\frac{dZ22}{dZ_1},\quad ZD222=\frac{dZ22}{dZ_2},\cdots,\quad ZDN22=\frac{dZ22}{dZ_n}$$

$$ZP222=\frac{dZ22}{dP_2},\quad ZP322=\frac{dZ22}{dP_3},\cdots,\quad ZPN22=\frac{dZ22}{dP_n}$$

where $Z_1, Z_2, \cdots, Z_n$ and $P_2, P_3, \cdots, P_n$ (set $P_1 = 0$) are flip angle β_i and phase angle $\varphi_i (i=1,\cdots,n)$, respectively. Minimization of function Z22 and its first derivatives (flips angles and phase angles) on the multidimensional space with respect to the resonance offset ($\Delta\omega/\omega_1$) could be carried out by commercially available routines, which solve a nonlinear least squares problem subject to bounds on the variables using modified Levenberg-Marguardt algorithm[11] in search of the global mininum corresponding to the "best" set of parameter values.

Designing the numerical solutions of equation (2) by allowing the starting parameters to take any values (flip angles and phase angles) vs resonance offset ($\Delta\omega/\omega_1$), new parameters of flip and phase angles can be obtained. Altering the resonance offset ($\Delta\omega/\omega_1$) and inputting the new parameters will lead the desired performance to be achieved.

Those steps involved in the analytical and numerical approach are as follows

(1) calculate the function Z22 and its first derivatives ZD122, ZD222, ⋯, ZDN22 (pulse flip angles), ZP222, ZP322, ⋯, ZPN22 (pulse phase angles) by means of the REDUCE program.

(2) use main FORTRAN program and subroutines Z22. FOR (function), ZD122. FOR, ZD222. FOR, ···, ZDN22. FOR and ZP222. FOR, ZP322. FOR, ···, ZPN22. FOR (first derivatives), as well as an "IMSL" Library DBCLSJ[11] to minimize guess pulse flip angles and phase angles with respect to the condition $M_Z = -1$ over a range of resonance offset ($\Delta\omega/\omega_1$).

(3) repeat the step (2) with a new pulse flip angles and phase angles by increasing a small range of resonance offset ($\Delta\omega/\omega_1$). This is repeated as many times as required until the desired performance is achieved.

By using the above mentioned method, composice π pulses with phase-distortion of two- and three-components are calculated, the results are summarized in Table 1.

Unfortunately, for four-composite pulse sequences, minimizing function and its derivatives will be carried out on a seven-dimensional parameter space ($\varphi_1 = 0$), there will be more than 10,000 lines of FORTRAN code, it is far beyond our present computer memory. Therefore, in this study, the production of Wigner matrices is calculated by the numerical method instead of its analytical expression. The version of this program uses only function Z22 (new function), and can be extended to any number of composite π pulses by simply changing the dimension. The calculations are divided into follewing two steps

(1) use main FORTRAN program and subroutine NZ22. FOR (New function), as well as an "IMSL" Library DBCLSF[12] to minimize guess flip angles and phase angles *via* range of resonance offset ($\Delta\omega/\omega_1$).

(2) increase resonance offset ($\Delta\omega/\omega_1$) and repeat step (1) with a new flip angles and phase angles as many times as required, until the optimized results are obtained.

Minimizing the composite π pulses by the numerical method requires relatively little computing time and efforts.

Table 1 Composite π pulses with phase distortion for ultra-broadband inversion

Number of component (N)	Sequence (deg.)	$\Delta\omega/\omega_1$	Total length compared with a simple pulse	ref.
1	180_0	±0.12	1	8
2	$198_0 382_{204}$	±0.7	5.8	13
	$183_0 370_{210}$	±0.7	5.8	this paper
3	$79_0 276_{180} 79_0$	±0.4	3.3	8
	$180_0 180_{120} 180_0$	±0.41	3.4	15
	$84_{94} 251_0 84_{44}$	±0.55	4.6	14
	$90_0 240_{90} 90_0$	±0.6	5.0	16,17
	$260_0 161_{190} 85_4$	±1.25	10.4	This paper
	$86_0 160_{180} 260_0$	±1.25	10.4	this paper
4	$64_0 146_{185} 320_{310} 77_{192}$	±0.4	3.3	8
	$180_0 180_{105} 180_{210} 360_{60}$	±0.6	5.0	18
	$52.5_0 72.8_{228.7} 72.3_{122} 197.6_{26}$	±1.45	12.1	This paper
5	$63_0 140_{140} 320_{240} 140_{140} 63_0$	±0.43	3.6	8
	$64_{32.2} 122_{96} 310_0 122_{96} 64_{322}$	±0.68	5.7	14
	$45_0 180_{90} 90_{180} 180_{90} 45_0$	±0.8	6.7	18
	$56.5_0 93.4_{153.4} 79.4_{18.7} 115.1_{203.0} 131.4_{120.9}$	±1.8	15	This paper
6	$52_0 94_{130} 66_{198} 323_{251} 143_{150} 63_{10}$	±0.47	3.9	8
	$107.6_0 177_{200} 68.6_{107.0} 54.1_{338.4} 109.8_{190.3} 298.8_{37.2}$	±2.0	16.7	This paper
7	$54_0 135_{183} 177_{296} 381_{11} 177_{296} 135_{183} 54_0$	±0.5	4.2	8
	$336_0 246_{180} 10_{90} 74_{270} 10_{90} 246_{180} 336_0$	±0.6	5.0	15
	$88.8_0 91.8_{117.4}$ 89.3_{310} $296.2_{130.5}$ $128.7_{320.3}$ $68.7_{248.2}$ $180.4_{21.2}$	±2.1	18	This paper
	$113.6_0 190.2_{177}$ $72.8_{86.0}$ $57.8_{340.1}$ $59.4_{210.6}$ $155_{43.7}$ $267.1_{288.2}$	±2.1	18	This paper
8	$77.2_0 75_{147}$ $74_{340.3}$ 201.8_{208} 110.7_{92} $116_{273.7}$ $67.6_{91.8}$ $266.1_{23.4}$	±2.4	20	This paper

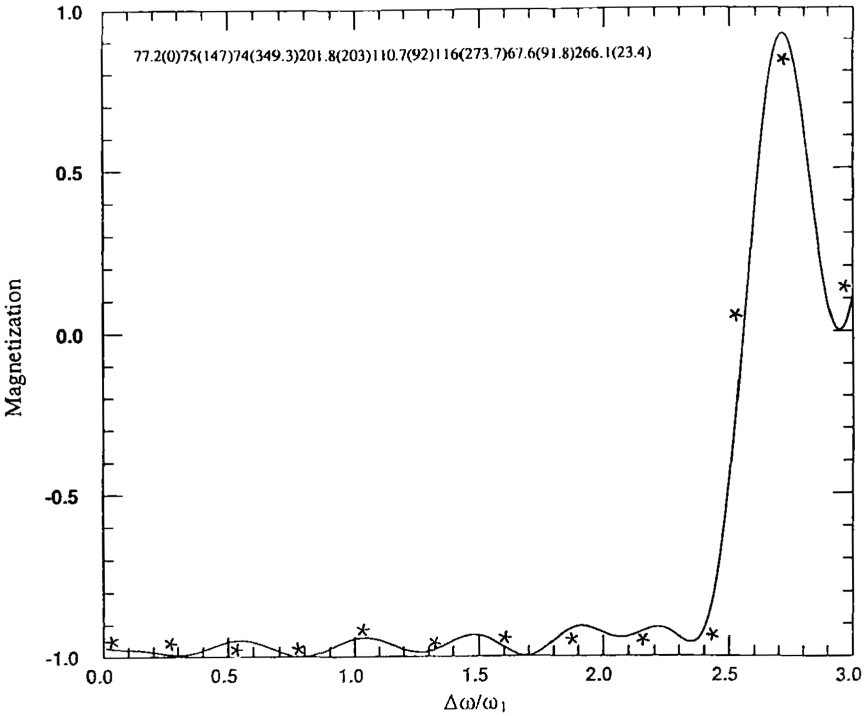

Fig. 1 Composite pulse of eight-sequence with phase distortion
(* experimental points)

In order to verify the new method, the data from reference[13] were used as a test example, it was found that the results of the new method were in good agreement with those reported in the reference. Calculations were run on an IBM/3600 computer.

RESULTS AND DISCUSSIONS

Composite π pulses with phase-distortion were constructed by the multipole theory approach, using the components of the magneti-

zation vector, M_Z, with respect to resonance offset($\Delta\omega/\omega_1$). For better two-, three-, four-, five-, six-, seven- and eight-component pulses, the final minimizing results are listed in Table 1.

A representative composite π pulse of eight-sequence 77.2(0) 75 (147) 74(349.3) 201.8(203) 110.7(92.0) 116(273.7) 67.6(91.8) 266.1(23.4), $|\Delta\omega/\omega_1| \cong 2.4$ is shown in Figure 1, the stars on the Figure 1 represent the experimental points.

Data were measured on a Varian VXR 500S NMR spectrometer for a 2% H_2O sample in D_2O lightly dropped with relaxation agent $Cr(acac)_3$, at a radio-frequency field strength of 1.22 KHz for line inversion. The experimental results agreed well with those obtained by calculations. Furthermore, the sequences are more robust about 1° than the theoretically predicted sequences. All of the results are better than those obtained by existing sequences. To our knowledge, there are no any analogous sequences that better than this method have so far been reported.

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