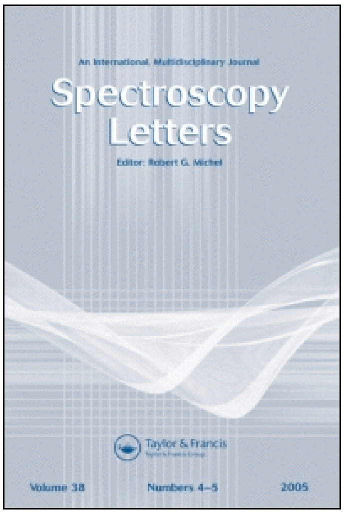

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Numerical Design of Composite Pulse NMR

Xujie Yang[a]; Xiaobo Huang[a]; Daoyong Chen[a]; Zhengliang Zhi[a]; Lude Lu[a]; Xin Wang[a]; B. C. Sanctuary[b]
[a] Materials Chemistry Laboratory, Nanjing University of Science and Technology, Nanjing, P. R. China
[b] Department of Chemistry, McGill University, Montreal, Canada

To cite this Article Yang, Xujie , Huang, Xiaobo , Chen, Daoyong , Zhi, Zhengliang , Lu, Lude , Wang, Xin and Sanctuary, B. C.(1998) 'Numerical Design of Composite Pulse NMR', Spectroscopy Letters, 31: 7, 1547 — 1555
To link to this Article: DOI: 10.1080/00387019808001659
URL: http://dx.doi.org/10.1080/00387019808001659

SPECTROSCOPY LETTERS, 31(7), 1547-1555 (1998)

Numerical Design of Composite Pulse NMR

Xujie Yang, Xiaobo Huang, Daoyong Chen, Zhengliang Zhi
Lude Lu and Xin Wang*
Materials Chemistry Laboratory, Nanjing University of Science and Technology, Nanjing 210094, *P. R. China*
B. C. Sanctuary
Department of Chemistry, McGill University, 801 *Sherbrooke Street West, Montreal, Quebec H*3*A* 2*K*6, *Canada*

ABSTRACT This paper describes the method of a phase-alternating composite π pulse sequences, in which the subroutines are programed instead of the previously reported "IMSL" library DUNSJ to solve the non-linear least square problems, being used to minimize the pulse angles with respect to resonance off-set. The main program and subroutines were carried out on a personal computer. It is found that the results from the new program were in agreement with that reported in the reference being obtained from IBM/3600 computer and the present method is more effeciant than other existing pulse sequences.

* Author to whom correspodence should be addressed

INTRODUCTION

The development of composite pulse as a means in NMR optimization could compensate for verious inadequacies of single pulse. In this respect, Freeman and Levitt[1] first proposed the composite sequences, since then composite pulses are used in many NMR experiments, including Hetero-TOCSY experiment with radio-frequency mixing pulse sequences[2], description of two-dimesional NMR experiment[3], assignment of the proton NMR spectra[4], and optimization of pulse sequences for studying biological macromolecules[5], among many other applications.

The design of composite pulses could be assisted by computer simulation of the paths of magnetization vectors during the sequence of pulses[6,7]. A numerical algorithm has been used in minimizing flip and phase angles with respect to off-resonance[8]. This paper describes of method of composite π pulse sequences with phase-alternating. The composite π pulse sequences are intended to flip the magnetization to antiparallel position, in which the phase function φ_i for i-th pulse is restricted to the values of 0 or π.

THEORY

Composite pulses exploit the group properties of rotations i. e., the product of n rotations will produce a new rotation,

$$D(\Omega) = \prod_{i=1}^{n} D(\Omega_i) \tag{1}$$

where Ω denotes the Eular angles, which can be expressed as[9]

$$\Omega_i = (\alpha_i + \varphi_i, \ \beta_i, \ \alpha_i - \varphi_i + \pi) \tag{2}$$

where β is the flip angle, α the azimuthal angle and φ pulse phase angle, which are given by

$$\begin{aligned} \sin\alpha &= -\cos(\Omega t/2)/\cos(\beta/2) \\ \cos\alpha &= -\Delta\omega/\Omega \cdot [\sin(\Omega t/2)/\cos(\beta/2)] \\ \sin\beta &= 2\omega_1/\Omega \cdot [\sin(\Omega t/2) \cdot \cos(\beta/2)] \\ \cos\beta &= 1/\Omega^2 \cdot [\Delta\omega^2 + \omega_1 \cos(\Omega t)] \end{aligned} \quad (3)$$

where $\Delta\omega = \omega - \omega_0$, $\omega_0 = \gamma H_z$, $\Omega = \sqrt{\Delta\omega^2 + \omega_1^2}$ and ω_j is the RF amplitude.

In general, composite pulses can be expressed as a Wigner rotation matrix acting on the nuclear spin polarizations, expressed as spherical tensor components[10]

$$\hat{\Phi}_q^k(t) = \sum_{q_1,q_2,\cdots q'} D_{qq_1}^{(k)}(\Omega_1) \cdot D_{q_1q_2}^{(k)}(\Omega_2) \cdots D_{q_{n-2}q_{n-1}}^{(k)}(\Omega_{n-1}) \cdot D_{q_{n-1}q'}^{(k)}(\Omega_n) \hat{\Phi}_{q'}^k(0) \quad (4)$$

where k is the tensor rank and q the spherical component. In addition, the $\hat{\Phi}_{q'}^k(0)$ is the multipole polarization at equilibrium and $\hat{\Phi}_q^k(t)$ the polarization at time t which representing the magnetization at Z direction.

On-resonance, α is reduced to the value of $-\pi/2$, and off-resonance, β and α are needed to fully describe pulses. For phase-alternating composite π pulses ($\varphi_{i+1} = \varphi_i + \pi$, $i = 1, 2, \cdots n$, set $\varphi_i = 0$), only the vector magnetization is treated, $k = 1$, $q = 0, \pm 1$. A composite pulse sequences containing n pulses is then simply expressed as a product of Wigner rotation matrix.

Extension of this method to multiple pulses can be carried out analytically by using computer algebra to multiply n rotation matrices together. In this case, non-linear least-square method has been used to optimize the flip angles of n composite pulses with respect to off-resonance ($\Delta\omega_i/\omega_1$).

For a phase-alternating composite π pulses considering the pulse angles is described by n parameters. The efficiency of a com-

Table 1 Optimizing procedures of three composite pulses

```
STARTING GUESSES ARE:
  .7650000D+02  .1813000D+03  .2869000D+03

NUMBER OF PTS IS  8  NUMBER OF PULSES IS  3
NUMBER OF OBJECT IS  3

GRADIENTS OF THE ANGLES ARE:
 -.1517204D-03 -.1642678D-03  .1016550D-03

THE RESIDUES ARE:

                  RESIDUES         DEL

                .2691891D-02  .0000000D+00
                .2956424D-02  .1000000D+00
                .2647161D-02  .2000000D+00
                .1246550D-02  .3000000D+00
                .1328477D-02  .4000000D+00
                .3835619D-02  .5000000D+00
                .4205373D-02  .6000000D+00
                .4338331D-02  .7000000D+00

FSUMSQ IS  .7791723D-04   FITTED ANGLES ARE:
  .8755122D+02  .2268343D+03  .3234880D+03

***********************************************

STARTING GUESSES ARE:
  .8760000D+02  .2268000D+03  .3235000D+03

NUMBER OF PTS IS 10  NUMBER OF PULSES IS  3
NUMBER OF OBJECT IS  3

GRADIENTS OF THE ANGLES ARE:
  .1208731D-03 -.1491438D-03  .9952606D-04

THE RESIDUES ARE:

                  RESIDUES         DEL

                .4960935D-02  .0000000D+00
                .7750708D-02  .1000000D+00
```

Table 1. Continued

.1163927D-01	.2000000D+00
.9778120D-02	.3000000D+00
.3712596D-02	.4000000D+00
.2658226D-02	.5000000D+00
.9977567D-02	.6000000D+00
.1511844D-01	.7000000D+00
.9175706D-02	.8000000D+00
.1675950D-01	.9000000D+00

FSUMSQ IS .1029812D-02 FITTED ANGLES ARE:
.8664927D+02 .2054029D+03 .3044631D+03

****

STARTING GUESSES ARE:
.8660000D+02 .2054000D+03 .3045000D+03

NUMBER OF PTS IS 12 NUMBER OF PULSES IS 3
NUMBER OF OBJECT IS 3

GRADIENTS OF THE ANGLES ARE:
-.4207138D-04 .1091601D-03 -.7447743D-04

THE RESIDUES ARE:

RESIDUES	DEL
.5764632D-02	.0000000D+00
.1365126D-01	.1000000D+00
.2858417D-01	.2000000D+00
.3377475D-01	.3000000D+00
.2287773D-01	.4000000D+00
.8055874D-02	.5000000D+00
.7758024D-02	.6000000D+00
.2523750D-01	.7000000D+00
.4147113D-01	.8000000D+00
.3479590D-01	.9000000D+00
.1646907D-01	.1000000D+01
.4826121D-01	.1100000D+01

FSUMSQ IS .8996292D-02 FITTED ANGLES ARE:
.8437175D+02 .1850756D+03 .2868589D+03

posite pulse may be characterized by function $F(\mathbf{x})$, being defined as[8]

$$F(\mathbf{x})=\sum_{i=1}^{m}[f(\mathbf{x})]^2=f(\mathbf{x})^T\cdot f(\mathbf{x}) \tag{5}$$
$$\mathbf{x}=(\beta_1,\beta_2,\cdots\beta_n)^T$$

where $m\geqslant n$, and $f_i(\mathbf{x})$ is the i-th component function $F(\mathbf{x})$. In this case, the optimized pulse sequences can be obtained by minimizing the function $F(\mathbf{x})$, which is termed cost function and the condition of minimum point must be satisfied.

$$g(\mathbf{x})=\nabla F(\mathbf{x})=Df(\mathbf{x})^T\cdot f(\mathbf{x})=0 \tag{6}$$

by a series of mathematical treatment, the following relationship for iteration can be obtained. More detailed information was given by Dennis[11] and Gill[12].

$$\begin{cases}X_{k+1}=X_k+P_k\\ P_k=-(J_k{}^TJ_k+\mu_kI)^{-1}\{J_k{}^Tf(\mathbf{x}_k)\}\end{cases} \tag{7}$$

where J is m x n Jacobian matrix $(J_{ij}=\partial f_i/\partial x_j)$, μ_k a damping factor of some non-negative value, and I unit matrix.

In eq. (7), the μ_k introduces a bias towards the steepest descent direction. It has been proven that, if the first derivative vector of $F(\mathbf{x})$ is uniformly continuous function for $F(\mathbf{x}_{k+1})\leqslant F(\mathbf{x}_k)$, then one can choose $\mu_k(k=1,2\cdots)$ so that g_k coverages to near zero. The condition assigned for the completion of minimization is cheeked. The condition is

$$\| g(\mathbf{x}_k)\| \leqslant\varepsilon \tag{8}$$

where ε is a gradient tolerance. This process is repeated many times until the minimization criterion is achieved.

CALCULATION AND RESULTS

We have reported a phase-alternating composite π pulse NMR[13], in which the "IMSL" library DUNSJ[14], solving the non-

Table 2 Optimized Phase-Alternating Composite π Pulse

Composite pulse	DEL ($\Delta\omega/\omega_1$)	Total rotation (degrees)	Reference
180	± 0.12	180	7
180	± 0.2	180	This paper
59.3 $\overline{220.2}$	± 0.5	279.5	13
84.7 $\overline{251.7}$	± 0.5	336.4	This paper
83.1 $\overline{175.5}$ 278.3	± 1.1	536.9	13
84.4 $\overline{185.1}$ 286.8	± 1.15	556.3	This paper
59 $\overline{298}$ 59	± 0.15	416	7
34.2 $\overline{123}$ 197.6 $\overline{288.8}$	± 1.0	643.6	15
37.9 $\overline{113.6}$ 167.5 $\overline{257.7}$	± 1.3	576.7	This paper
58 $\overline{140}$ 344 $\overline{140}$ 58	± 0.35	740	7
51 $\overline{113.4}$ 296.4 $\overline{113.4}$ 51	± 0.7	921.6	This paper
389.2 $\overline{176.3}$ 108.9 $\overline{287.6}$ 156.5	± 1.4	1118.5	This paper
158 $\overline{171.2}$ 342.8 $\overline{145.5}$ 81.2 $\overline{85.3}$	± 1.5	984	15
143.3 $\overline{154.1}$ 320.9 $\overline{121.8}$ 72.2 $\overline{84.3}$	± 1.8	896.6	This paper
131.6 $\overline{142.2}$ 314.8 $\overline{115.1}$ 70.2 $\overline{83.4}$	± 1.8	857.3	13
66 $\overline{180}$ 227 $\overline{406}$ 227 $\overline{180}$ 66	± 0.85	1420	7
80.5 $\overline{67.2}$ 115.7 $\overline{310.1}$ 144.2 $\overline{150.8}$ 11.1	± 1.9	879.6	13
84.3 $\overline{72.2}$ 121.8 $\overline{320.9}$ 154.1 $\overline{143.7}$ 0.33	± 1.8	897.3	This paper
91.6 $\overline{64.4}$ 124.4 $\overline{112.4}$ 8.5 $\overline{311.3}$ 143 $\overline{157.2}$	± 2.0	912.3	13
69.1 $\overline{100.6}$ 96.4 $\overline{158.1}$ 199.8 $\overline{69.9}$ 45.6 $\overline{249.4}$	± 2.0	988.8	This paper

linear least square problems, has been used to optimize pulse angles with respect to a range of resonance off-set ($\Delta\omega_i/\omega_1$). In this paper, we present an algorithm for the least-squares estimation of non-linear parameters instead of the "IMSL" library DUNSJ. Calculation were carried out on COMPAQ 586 personal computer. The optimization of F(**x**) with respect to the parameters **x** including pulse angles and resonance off-set was performed. The optimizing steps are as follows.

(1) program subroutine DBSLS and SOLEQ were used to calculate $f(\mathbf{x}_k)$, J_k, g_k, $F(\mathbf{x}_k)$ and $(J_k^TJ_k+\mu_kI)P_k=-J_k^Tf(\mathbf{x}_k)$, respectively.

(2) a main program and subroutine DBSLS and SOLEQ were used to optimize pulse angles in the range of resonance off-set ($\Delta\omega_i/\omega_1$) called DEL.

(3) repeat step(2) with optimized pulse angles by means of increasing the off-set ($\Delta\omega_i/\omega_1$), until the required results are obtained. The optimized procedures of three composite π pulses (76.5° 181.3° 286.9°) are listed in Table 1.

(4) after above steps, the final optimized data of other composite pulse angles are summerized in Table 2. It is found that the results are in good agreement with those reported in the reference[13], the present method is more effeciant than other composite pulse sequences.

ACKNOWLEDGMENTS

The support of this work by grants from the Natural Science Foundation of Jiangsu (China), and the Provincial Government of Quebec (Canada) is gratefully acnowledged.

REFERENCES

1. Freeman, R. and Levitt, M. H., *J. Magn. Reson.*, 1979, 33, 73
2. Brown, L. R. and Sanctuary, B. C., *J. Mang. Reson.*, 1991, 91, 413
3. Kayters, R. P. E., Char, B. W. and Addison, A. W., *J. Magn. Reson.*, 1993, 101, 276
4. Yu, C., Hwang, J. F., Chen, T. B. and Soo, V. W., *J. Chem. Inform. and Comput. Sci.*, 1992, 32, 183
5. Price, W. S., Hayamizu, K. and Arata, Y., *J. Magn. Reson*, 1997, 126, 256
6. Levitt, M. H., *J. Magn. Reson.*, 1982, 48, 234
7. Shaka, A. J. and Pines, A., *J. Magn. Reson.*, 1987, 71, 495
8. Lurie, D. J., *J. Magn. Reson.*, 1986, 70, 11
9. Yang, X. J., Keniry, M. A. and Sanctuary B. C., *J. Magn. Reson.*, 1993, 105A, 295
10. Lee, N., Lam. M. E. and Sanctuary, B. C., *J. Magn. Reson.*, 1991, 92, 455
11. Dennis, J. E. and Robert, B. C., *Numerical Methods for Unconstrained Optimization and Nonlinear Equations*, 1983, Prentice-Hall, Englewood cliffs, New Jersey
12. Gill, P. E. and Murray, W., *SLAM J. Numer. Anal.*, 1978, 15 (5), 977
13. Yang, X. J., Lu, L. D. and Wang, X., *Spectroscopy Letts.*, 1995, 8, 1191
14. IMSL Math/Library FORTRAN Subroutines for Mathematical Applications, 1987, 841, IMSL Inc.
15. Shaka, A. J., *Chem. Phys. Lett.*, 1985, 120, 201

Date Received: April 29, 1998
Date Accepted: June 2, 1998