Pramana–J. Phys., Vol. 36, No. 4, April 1991, pp. 399–406. © Printed in India.

Phase-alternated composite $\pi/2$ pulses for solid state quadrupole echo NMR spectroscopy

A RAMAMOORTHY* and P T NARASIMHAN†

Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India
Present address:
*Laboratory of Chemical Physics, Central Leather Research Institute, Adayar, Tamil Nadu 600020, India
†Huntington Medical Research Institutes and Department of Chemistry, Magnetic Resonance Spectroscopy Division, 660 S. Fair Oaks, Pasadena, CA 91125, USA

MS received 19 September 1990; revised 1 December 1990

Abstract. Phase-alternated composite $\pi/2$ pulses have been constructed for spin $I = 1$ to overcome quadrupole interaction effects in solid state nuclear magnetic resonance (NMR) spectroscopy. Magnus expansion approach is used to design these sequences in a manner similar to the NMR coherent averaging theory. It is inferred that the symmetric phase-alternated composite $\pi/2$ pulses reported here are quite successful in producing quadrupole echo free from phase distortions. This effectiveness of the present composite pulses is due to the fact that most of them are of shorter durations as compared to the ones reported in literature. In this theoretical procedure, irreducible spherical tensor operator formalism is employed to simplify the complexity involved in the evaluation of Magnus expansion terms. It has been argued in this paper that composite $\pi/2$ pulse sequences for this purpose can also be derived from the broadband inversion π pulses which are designed to compensate electric field gradient (*efg*) inhomogeneity in spin $I = 1$ nuclear quadrupole resonance (NQR) spectroscopy.

Keywords. Nuclear magnetic resonance; composite pulses; Magnus expansion; quadrupole echo; tensor operator; nuclear quadrupole resonance.

PACS No. 76·60

1. Introduction

In solid state NMR spectroscopy of spin $I = 1$ nuclei, spectral lines are generally broad because of the presence of nuclear quadrupole (ω_Q) and dipole–dipole (ω_D) interactions (Abragam 1961). In addition to this, the influence of the quadrupole interaction during radiofrequency (rf) pulses of finite duration and limited power leads to severe distortions in the powder line shape (Bloom *et al* 1980). This problem may be partly overcome by the application of short duration rf pulses with either high rf power (Siminovitch and Griffin 1985; Hiyama *et al* 1986) or smaller flip angle. Increasing the rf power indefinitely is not possible because of the technical problems, affecting the transmitter and the probe, whereas small flip angles lead to poor signal intensity. Therefore, the task of achieving uniform excitation over the range of line broadening interactions, quadrupole interaction in particular, is difficult using a single rf pulse. To some extent, these distortions have been overcome by replacing single rf pulses with composite pulses (Levitt *et al* 1986). Composite pulses are a train of rf pulses, applied without any time delay between them but may be with different phases and durations. Tycko and co-workers (1983, 1984) were the first to construct composite π pulses using the Magnus expansion approximation (Magnus 1954) for broadband population inversion over large ranges of ω_Q and ω_D. It should be mentioned here that composite $\pi/2$ pulses are also important in quadrupole echo experiments (Solomon 1958; Davis *et al* 1976). The purpose of using quadrupole echo technique is to circumvent the deadtime problem associated with single pulse experiments (Abragam 1961). Furthermore, quadrupole echo method especially in ^{2}H-NMR, has become a powerful means for probing dynamic processes in polymers (Davis *et al* 1976; Hentschel and Spiess 1979; Seeling 1977; Griffin 1981; Spiess 1983). It would therefore be very useful to construct composite $\pi/2$ pulses for achieving quadrupole echo without phase distortions. In this context, Levitt *et al* (1986) have showed how certain inversion composite pulses designed for spin $I = 1/2$ systems could be converted to useful $I = 1$ composite $\pi/2$ pulses. Siminovitch *et al* (1986) examined several composite pulses experimentally and they concluded that these sequences also introduce additional distortions with the reduction of finite pulse width effects. Later, Dongsheng *et al* (1987) constructed higher order composite $\pi/2$ pulses for quadrupole echo without phase distortions but only at the expense of increasing the excitation period. These sequences will not be of much use because effects of chemical exchange during composite pulses introduce additional complications in the interpretation and analysis of lineshape in solid state NMR (Siminovitch *et al* 1986; Barbara *et al* 1986). Recently, some important composite $\pi/2$ and π pulses have been proposed for this purpose by Raleigh *et al* (1989).

The aim of this work is to construct short duration composite $\pi/2$ pulses for spin $I = 1$ NMR by the Magnus expansion approach (Tycko 1983) to obtain quadrupole echo without phase distortions. Here the irreducible spherical tensor operators (Bowden and Hutchison 1986) are employed to evaluate the Magnus expansion terms. The organization of this paper is as follows. In § 2, the Hamiltonians of various interactions present in the system is described. Derivation of the zeroth-order composite pulses using the Magnus expansion method is briefly given in § 3, while § 4 highlights the performance of composite $\pi/2$ pulses. Conclusions of this work are presented in § 5.

2. Hamiltonian of the system of spin $I = 1$ nuclei

Consider an ensemble of spin $I = 1$ nuclei in the presence of a static magnetic field that defines the laboratory frame Z-axis. The total Hamiltonian of this spin system in the rotating frame of NMR is given by

$$\mathscr{H} = \mathscr{H}_{\rm rf} + \mathscr{H}_Q \tag{1}$$

where $\mathscr{H}_{\rm rf}$ is the interaction of the spin system with rf radiation of strength ω_1 (rad/sec) and phase $\phi(t)$ applied in the XY-plane of the laboratory frame. It can be written as

$$\mathscr{H}_{\rm rf} = -\omega_1 [I_x \cos\phi(t) + I_y \sin\phi(t)] \tag{2}$$

where $I_p(x, y, z)$ are components of spin angular momentum operator. Using the tensor operators (Bowden and Hutchison 1986), (2) can be expressed as

$$\mathscr{H}_{rf} = \omega_1 [T_1^1(a)\cos\phi(t) - iT_1^1(s)\sin\phi(t)] \tag{3}$$

where $T_m^l(a,s)$ are irreducible spherical tensor operators (more about it is given in the Appendix). The quadrupole coupling seen by a given spin can in first order be replaced by its part $\mathscr{H}_Q$ that commutes with the Zeeman Hamiltonian $\mathscr{H}_Z = -\omega_0 I_z$, ω_0 is the Larmor frequency.

$$\mathscr{H}_Q = \omega_Q[I_z^2 - \tfrac{1}{3}I^2] \tag{4}$$

where ω_Q is the quadrupole coupling constant and it is expressed as

$$\omega_Q = \frac{e^2qQ}{4I(2I-1)}\left[\frac{1}{2}(3\cos^2\alpha - 1) + \eta\cos 2\beta\sin^2\alpha\right] \tag{5}$$

where α and β are the polar angles which defines the direction of the Zeeman field with respect to the crystalline frame. η describes the asymmetry present in the *efg* surrounding the quadrupole nuclei. In the next section, a brief discussion of the Magnus expansion technique to design composite pulses is given. Detailed procedure has been given elsewhere (Tycko 1983; Ramamoorthy and Narasimhan 1989).

3. Derivation of zeroth-order composite pulses using the Magnus expansion approach

The net evolution operator in the rotating frame can be given as (Tycko 1983)

$$U(t) = U_{rf}(t)U_Q(t) \tag{6}$$

where

$$U_{rf}(t) = T\exp[-i\mathscr{H}_{rf}(t)t] \tag{7}$$

and

$$U_Q(t) = T\exp\left[-i\int\tilde{\mathscr{H}}_Q(t')\,\mathrm{d}t'\right] \tag{8}$$

where T is the Dyson time-ordering operator and $\tilde{\mathscr{H}}_Q(t)$ is the total Hamiltonian in the rf interaction frame (Haeberlen 1976) which is defined by $U_{rf}(t)$, that is,

$$\tilde{\mathscr{H}}_Q(t) = U_{rf}(t)^{-1}\mathscr{H}_Q U_{rf}(t). \tag{9}$$

Here, only the phase alternating pulse sequence of the type $\theta_1\bar{\theta}_2\theta_3$ are considered which can be implemented in an experiment easily without the need for a sophisticated digital phase shifter. The overbar in our notation indicates that the corresponding rf pulse is 180° phase shifted with respect to unbarred rf pulses in the sequence. θ_n is the flip angle of the nth rf pulse with duration t_n as given by $\theta_n = \omega_1 t_n$.

The rf propagator $U_{rf}(t)$ can be written for an n-pulse sequence as

$$U_{rf}(t) = U_{rf_n}U_{rf_{n-1}}\cdots\cdots U_{rf_2}U_{rf_1} \tag{10}$$

where, from (2) and (7), we have

$$U_{rf_n} = \exp[\mp i\omega_1 T_1^1(a)t_n]. \tag{11}$$

In the above equation, the $-$ and $+$ signs correspond to the zero and 180° phases of rf pulses. $\tilde{\mathscr{H}}_Q(t)$ can be obtained from the transformation properties of tensor operators under the effect of the rf propagator $U_{rf}(t)$ (refer Appendix). The time dependent $\tilde{\mathscr{H}}_Q(t)$ can be written using the Magnus expansion (Magnus 1954) as

$$\tilde{\mathscr{H}}_Q(t) = \mathscr{H}_Q^0 + \mathscr{H}_Q^1 + \mathscr{H}_Q^2 + \dots \tag{12}$$

where $\mathscr{H}_Q^i$ is the ith order term in the Magnus expansion. Here, only the zeroth-order term in the Magnus expansion is considered because the inclusion of higher-order terms lead to larger duration (or more number of rf pulses) sequence; $\mathscr{H}_Q^0$ is given as (Haeberlen 1976),

$$\mathscr{H}_Q^0 = \frac{1}{t}\int_0^t \tilde{\mathscr{H}}_Q(t')\,\mathrm{d}t'. \tag{13}$$

For a pulse sequence of the type $\theta_1\bar{\theta}_2\theta_3$, one can write $\mathscr{H}_Q^0$ to be

$$\mathscr{H}_Q^0 = \frac{\sqrt{2}\omega_Q}{\sqrt{3}\omega_1 t}[aT_0^2 + biT_1^2(s) + cT_2^2(s)] \tag{14}$$

where

$$a = \frac{3}{4}\left[\frac{(\theta_1+\theta_2+\theta_3)}{3} + \sin 2\theta_1 + \sin(2\theta_2 - 2\theta_1) + \frac{1}{2}\sin(2\theta_3 - 2\theta_2 + 2\theta_1)\right] \tag{15}$$

$$b = \frac{\sqrt{3}}{4}[1 - 2\cos 2\theta_1 + 2\cos(2\theta_1 - 2\theta_2) - \cos(2\theta_1 + 2\theta_3 - 2\theta_2)] \tag{16}$$

$$c = \frac{\sqrt{3}}{8}[-(\theta_1+\theta_2+\theta_3) + 2\sin 2\theta_1 + 2\sin(2\theta_2 - 2\theta_1) + \sin(2\theta_1 + 2\theta_3 - 2\theta_2)] \tag{17}$$

According to the Magnus expansion technique (Tycko *et al* 1983, 1984), a zeroth order composite pulse can be obtained by selecting flip angle values in such a way that the sequence satisfies the condition, i.e., $\mathscr{H}_Q^0 = 0$. For this sequence, $U_Q = 1$, thus one can achieve uniform excitation over larger range of ω_Q. From (15)–(17) one can say that it is not possible to satisfy this condition with a three pulse phase alternated sequence. So, the condition is relaxed to

$$[\mathscr{H}_Q^0, \rho(0)] = 0 \tag{18}$$

where $\rho(0) = \omega_0 I_z$ is the thermal equilibrium density matrix. This condition demands only 'b' given by (16) to be equal to zero because in $\mathscr{H}_Q^0$, T_0^2 and $T_2^2(s)$ commute with $\rho(0)$ but $[T_1^2(s), \rho(0)] \neq 0$. A set of zeroth-order composite $\pi/2$ pulses derived with $b = 0$ and with smaller size 'b' have been summarized in table 1 alongwith the corresponding zeroth-order Magnus terms. Interestingly, when the durations of individual pulses in the sequence given in table 1 are doubled, one gets a set of composite π pulses for NQR spectroscopy of spin $I = 1$ nuclei (Ramamoorthy 1989; Ramamoorthy and Narasimhan 1991) which compensate for the *efg* inhomogeneity. It is noteworthy that any pulse sequence involving phase shifts only in multiples of

Table 1. Composite $\pi/2$ pulses with their zeroth-order Magnus expansion terms and their bandwidth of uniform excitation over ω_Q.

Composite $\pi/2$ pulse	Bandwidth[a]	$\frac{\omega_1 t}{\omega_Q}\mathscr{H}_Q^0$
1. 130 $\overline{80}$ 40	$\pm 1{\cdot}4$	$-0{\cdot}315\ T_0^2 + 0{\cdot}707 iT_1^2(s) - 1{\cdot}468\ T_2^2(s)$
2. 157·5 $\overline{112{\cdot}5}$ 45	$\pm 0{\cdot}8$	$0{\cdot}077\ T_0^2 + 0{\cdot}207 iT_1^2(s) - 2{\cdot}73\ T_2^2(s)$
3. 130 $\overline{40}$	$\pm 0{\cdot}4$	$0{\cdot}003\ T_0^2 + 0{\cdot}123 iT_1^2(s) - 0{\cdot}873\ T_2^2(s)$
4. $\overline{22{\cdot}5}$ 112·5	$\pm 0{\cdot}25$	$0{\cdot}914\ T_0^2 - 0{\cdot}15 iT_1^2(s) - 0{\cdot}167\ T_2^2(s)$
5. $\overline{60}$ 150	$\pm 0{\cdot}25$	$1{\cdot}278\ T_0^2 + 0{\cdot}354 iT_1^2(s) - 0{\cdot}342\ T_2^2(s)$
6. $\overline{30}$ 150 $\overline{30}$	$\pm 0{\cdot}4$	$0{\cdot}748\ T_0^2 - 0{\cdot}648\ T_2^2(s)$
7. $\overline{11{\cdot}25}$ 112·5 $\overline{11{\cdot}25}$	$\pm 0{\cdot}25$	$0{\cdot}481\ T_0^2 - 0{\cdot}599 iT_1^2(s) - 0{\cdot}417\ T_2^2(s)$

[a] In terms of the dimensionless quadrupole interaction parameter $\omega_Q/2\omega_1$ for which the echo amplitude is greater than 95% of the one corresponding to $\omega_Q = 0$ case.

π radians and which generates a broadband population inversion in two-level system will provide a broadband excitation in the anharmonic three-level system if the pulse duration is halved (Levitt *et al* 1984). Similarly, halving the individual pulse durations in a composite π pulse of spin $I = 1$ NQR case leads to a composite $\pi/2$ pulse in spin $I = 1$ NMR case problem. For example, from NQR composite π pulses namely, $\overline{60}$ 300 $\overline{60}$ and $\overline{22{\cdot}5}$ 225 $\overline{22{\cdot}5}$ (Ramamoorthy and Narasimhan 1989, 1991), one can derive composite $\pi/2$ pulses for the present problem as $\overline{30}$ 150 $\overline{30}$ and $\overline{11{\cdot}25}$ 112·5 $\overline{11{\cdot}25}$. It is well-known that an applied rf pulse always connects only two out of the three energy levels of $I = 1$ NQR case depending on the direction and frequency of the pulse (Vega 1975). From these concepts, we may conclude that spin $I = 1$ pure NQR case is basically a two-level problem.

In the next section the performance of composite $\pi/2$ pulses has been illustrated.

4. Performance of composite pulses

To test the efficiency of composite $\pi/2$ pulses, the analytical expressions for the amplitude and phase of the quadrupole echo reported by Barbara (1986) have been used for a three pulse sequence of the type $\theta_1 \bar{\theta}_2 \theta_3$. They can be given as follows:

$$\text{echo amplitude, } A = [A_1^2 + A_2^2]^{3/2} \tag{19}$$

and

$$\text{phase, } \phi = \tan^{-1}[A_2/A_1] \tag{20}$$

where

$$A_1 = [\cos\alpha_1 \cos\alpha_2 \sin\alpha_3 - \cos\alpha_3 \sin(\alpha_2 - \alpha_1)]\sin k - \sin\alpha_1 \sin\alpha_2 \sin\alpha_3 \sin 3k \tag{21}$$

$$A_2 = \sin 2k \sin\alpha_2 \sin(\alpha_3 - \alpha_1) \tag{22}$$

$$k = \tan^{-1}[2\omega_1/\omega_Q]. \tag{23}$$

where

$$\alpha_n = \theta_n(1 + \lambda^2)^{1/2}; \quad \lambda = \omega_Q/2\omega_1.$$

Table 2. Symmetric phase-alternated composite $\pi/2$ pulses for compensating quadrupole interaction in the case of spin $I = 1$ NMR spectroscopy.

1.	$171{\cdot}5\ \overline{140}\ 27\ \overline{140}\ 171{\cdot}5$
2.	$29\ \overline{70}\ 172\ \overline{70}\ 29$
3.	$162{\cdot}5\ \overline{131{\cdot}5}\ 28\ \overline{131{\cdot}5}\ 162{\cdot}5$
4.	$\overline{33}\ 90\ \overline{113{\cdot}5}\ 203\ \overline{113{\cdot}5}\ 90\ \overline{33}$
5.	$13{\cdot}5\ \overline{49{\cdot}5}\ 90\ \overline{105{\cdot}5}\ 193\ \overline{105{\cdot}5}\ 90\ \overline{49{\cdot}5}\ 13{\cdot}5$
6.	$79\ \overline{147}\ 72\ \overline{76}\ 145{\cdot}5\ \overline{44{\cdot}5}\ 32\ \overline{44{\cdot}5}\ 145{\cdot}5\ \overline{76}\ 72\ \overline{147}\ 79$

When $\theta_1 = \theta_3$, that is, for a symmetric phase alternating sequence of the form $\theta_1\bar{\theta}_2\theta_1$, $A_2 = 0$ and hence $\phi = 0$, irrespective of the strength of the quadrupole interaction, ω_Q. Hence, symmetric phase alternating composite $\pi/2$ pulses can be used for generating quadrupole echo without phase distortions. The performance of different composite $\pi/2$ pulses has been examined by evaluating the amplitude of quadrupole echo with respect to ω_Q. Their bandwidth of uniform excitation is summarized in table 1 for which the echo amplitude is greater than 95% of the echo amplitude with no quadrupole interactions. Admittedly, the degree of compensation of ω_Q by these sequence is not very good. But one can construct symmetric sequences with a larger number of rf pulses so as to enhance the degree of compensation against ω_Q as well as to suppress phase distortions. Some of the composite $\pi/2$ sequences obtained for this purpose from two-level broadband inversion sequences (Shaka and Pines 1987; Ramamoorthy 1989; Ramamoorthy and Narasimhan 1989, 1991) are given in table 2. The case of line broadening due to the dipole-dipole interaction deserves a special mention here. The Hamiltonian can be expressed as (Abragam 1961)

$$\mathscr{H}_D = \sum_{i>j} d_{ij}\left[I_{zi}I_{zj} - \frac{1}{3}I_i \cdot I_j\right] \qquad (24)$$

where d_{ij} is the dipole-dipole coupling constant between spins i and j. It can easily be shown that the transformation property of $\mathscr{H}_D$ for an ensemble of two spin $I = 1/2$ coupled system under unitary evolutions is the same as that of $\mathscr{H}_Q$ in spin $I = 1$ case (Haeberlen 1976). Therefore, all these composite $\pi/2$ pulses which are derived for the quadrupole echo experiment can also be used for the uniform excitation of the ensemble of dipolar coupled spin $I = 1/2$ system over a wide range of ω_D.

5. Conclusions

Construction of phase alternated composite $\pi/2$ pulses for the use in solid state NMR spectroscopy using the Magnus expansion procedure is presented. It is important to note that the application of symmetric phase alternated composite $\pi/2$ pulses gives quadrupole echo with no phase distortions. Furthermore, these sequences behave like single rf pulses with a constant net flip angle of $\pi/2$ radians over larger range of ω_Q. The irreducible spherical tensors employed here simplifies the derivation of Magnus expansion terms and hence the design of composite pulses to a greater extent. It has been shown that phase-alternated composite $\pi/2$ pulses for a three-level case ($I = 1$ NMR case) can be derived from NQR phase alternated broadband inversion pulses which combat the effects of *efg* inhomogeneity. Hence, the design of composite pulses for spin $I = 1$ nuclei in NMR and NQR spectroscopies need not be considered separately. Results presented in this paper are also valid for an ensemble of two spin $I = 1/2$ nuclei coupled through dipole-dipole interaction.

Appendix

The tensor operator formalism in the form used by Bowden and Hutchison (1986) has been applied in this paper. They give the form and properties of these operators in detail. The symmetric $T^l_m(s)$ and antisymmetric $T^l_m(a)$ tensor combinations are given by

$$iT^l_m(s) = \frac{1}{\sqrt{2}}[T^l_m + T^l_{-m}] \tag{A1}$$

and

$$T^l_m(a) = \frac{1}{\sqrt{2}}[T^l_{+m} - T^l_{-m}] \tag{A2}$$

where l is the rank and m is the order of the tensor T^l_m. In this paper, the evolution of different tensors under the effect of an rf pulse has been obtained using the nested commutation relationship. That is

$$\begin{aligned}\tilde{\mathscr{H}}_Q(t) &= U_{rf}(t)^{-1}\mathscr{H}_Q U_{rf}(t) \\ &= \exp(i\mathscr{H}_{rf}t_n)\mathscr{H}_Q\exp(-i\mathscr{H}_{rf}t_n) \\ &= \mathscr{H}_Q + it_n[\mathscr{H}_{rf}, \mathscr{H}_Q] + \frac{(it_n)^2}{2!}[\mathscr{H}_{rf}, [\mathscr{H}_{rf}, \mathscr{H}_Q]] + \ldots\end{aligned} \tag{A3}$$

where $\mathscr{H}_{rf}$ is given by (3) of the text. Using the commutation relationships given by Bowden and Hutchison (1986), one can derive

$$\begin{aligned}U_{rf}(t)^{-1}T^2_0U_{rf}(t) = {} & T^2_0\frac{1}{4}[1 + 3\cos(2\omega_1 t_n)] - iT^2_1(s)\frac{\sqrt{3}}{2}\sin(2\omega_1 t_n) \\ & - T^2_2(s)\frac{\sqrt{3}}{4}[1 - \cos(2\omega_1 t_n)]\end{aligned} \tag{A4}$$

$$\begin{aligned}U_{rf}(t)^{-1}T^2_1(s)U_{rf}(t) = {} & -iT^2_0\frac{\sqrt{3}}{2}\sin(2\omega_1 t_n) + T^2_1(s)\cos(2\omega_1 t_n) \\ & - i/2\, T^2_2(s)\sin(2\omega_1 t_n)\end{aligned} \tag{A5}$$

$$\begin{aligned}U_{rf}(t)^{-1}T^2_2(s)U_{rf}(t) = {} & -T^2_0\frac{\sqrt{3}}{4}[1 - \cos(2\omega_1 t_n)] - i/2\, T^2_1(s)\sin(2\omega_1 t_n) \\ & + T^2_2(s)\frac{1}{4}[3 + \cos(2\omega_1 t_n)].\end{aligned} \tag{A6}$$

Using these transformation properties, $\tilde{\mathscr{H}}_Q(t)$ has been evaluated and the integration of $\tilde{\mathscr{H}}_Q(t)$ with respective time intervals of the pulse sequence leads to $\mathscr{H}_Q^0$ as given by (14) of the text. The advantage with the tensor operator formalism is that it forms a complete basis set and one needs to study the time-dependence of only three operators for the present work instead of the usual $(2I+1)^2-1$ operators. Hence, the theoretical treatment is simplified.

References

Abragam A 1961 *Principles of nuclear magnetism* (Oxford: University Press)
Barbara T M 1986 *J. Magn. Reson.* **67** 491
Barbara T M, Greenfield M S, Vold R L and Vold R R 1986 *J. Magn. Reson.* **69** 311
Bloom M, Davis J H and Valic M I 1980 *Can. J. Phys.* **58** 1510
Bowden G J and Hutchison W D 1986 *J. Magn. Reson.* **67** 403
Davis J H, Jeffrey K R, Bloom M, Valic M I and Higgs T P 1976 *Chem. Phys. Lett.* **42** 390
Davis J H 1981 *Biochim. Biophys. Acta* **737** 117
Dongsheng W, Gengying L and Xeuwen W 1987 *J. Magn. Reson.* **74** 464
Griffin R G 1983 *Meth. Enzymol.* **72** 108
Haeberlen U 1976 *High resolution NMR in solids: Selective averaging* (New York: Academic Press)
Hentschel R and Spiess H W 1979 *J. Magn. Reson.* **35** 157
Hiyama Y, Silverston J V, Torchia D A, Gerig J T and Hammond S J 1986 *J. Am. Chem. Soc.* **108** 2715
Levitt M H 1986 *Prog. NMR Spectrosc.* **18** 61
Levitt M H, Suter D and Ernst R R 1984 *J. Chem. Phys.* **80** 3064
Magnus W 1954 *Commun. Pure Appl. Math.* **7** 649
Raleigh D P, Olejniczak E T and Griffin R G 1989 *J. Magn. Reson.* **81** 455
Ramamoorthy A and Narasimhan P T 1989 *J. Mol. Struct.* **192** 333
Ramamoorthy A 1989 *Composite pulses for NQR spectroscopy*, Ph. D Thesis. Indian Institute of Technology, Kanpur, India
Ramamoorthy A and Narasimhan P T 1991 *Mol. Phys.* (in press)
Seelig J 1977 *Q. Rev. Biophys.* **10** 353
Shaka A J and Pines A 1987 *J. Magn. Reson.* **71** 495
Siminovitch D and Griffin R G 1985 *J. Magn. Reson.* **62** 99
Siminovitch D J, Raleigh D P, Olejniczak E T and Griffin R G 1986 *J. Chem. Phys.* **84** 2556
Solomon I 1958 *Phys. Rev.* **110** 61
Spiess H W 1983 *Colloid. Polym. Sci.* **261** 193
Tycko R 1983 *Phys. Rev. Lett.* **51** 775
Tycko R, Schneider E and Pines A 1984 *J. Chem. Phys.* **81** 680
Vega S 1975 *J. Chem. Phys.* **63** 3769