

# Revision of Spin Echoes in Pure Nuclear Quadrupole Resonance

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**Goldman's spin-1/2 formalism has been used for describing the response of an  $I = 3/2$  spin system to a two-pulse sequence in a pure nuclear quadrupole resonance experiment. A detailed analysis of the polarization evolution and quadrupolar echo generation is carried out through the use of explicit expressions for secular homo- and heteronuclear dipolar interactions. In striking contrast with previous studies, it is predicted that Van Vleck's second moments governing a classical solid-echo or Hahn sequence differ from those obtained by equivalent means in magnetic resonance. In fact, it is shown that, although measured moments still complement each other, the combined use of standard sequences does not allow the separate determination of homo- and heteronuclear dipolar contributions to the linewidth, not even in an indirect manner. In this context, the importance and potential usefulness of a crossed coil probe are also briefly discussed.** © 2001 Academic Press

**Key Words:** NQR; spin echoes.

## INTRODUCTION

Over several years, the analytic study of the response signal of an interacting nuclear quadrupolar system to a radiofrequency pulse has been delayed, largely due to the absence of a formalism capable of describing the problem in an appropriate manner. In 1977, Pratt (1) proposed a scheme for describing an  $I = 3/2$  system which was based on a triad of spin operators satisfying commutation rules similar to those valid for the Cartesian components of the angular momentum. In strong analogy to the situation found in magnetic resonance, this formalism allows an interaction representation, which facilitates the description of the density matrix evolution during the rf irradiation. However, the contribution due to the secular dipolar Hamiltonian cannot be entirely expressed as a function of these operators and has systematically led to an incorrect description of the echo signal following a pulse sequence in a pure nuclear quadrupole resonance experiment (2).

In this study, Goldman's spin-1/2 formalism (3) has been used to characterize the complex homo- and heteronuclear dipolar interactions governing the evolution of an  $I = 3/2$  nuclear spin system after an rf pulse. On this basis, the generation and gradual decay of the echo following a standard pulse sequence will be discussed.

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## THEORY

### (i) Quadrupolar Interaction

The Hamiltonian describing an  $I > 1/2$  spin ensemble in the presence of quadrupolar couplings has the form

$$H_Q = \frac{\omega_Q}{2} \sum_i \left( I_{zi}^2 - \frac{1}{3} I(I+1) \right); \quad \omega_Q = \frac{3e^2qQ}{2I(2I-1)}. \quad [1]$$

In this expression, the existence of a unique electric field gradient direction has been assumed and a laboratory reference system coinciding with the principal axes of the gradient tensor has been chosen. For simplicity's sake, an axially symmetric charge distribution around the nucleus of interest has been imposed, a situation often found in practical <sup>35</sup>Cl or <sup>79</sup>Br spectroscopy.

Given the strong versatility of the Pauli matrices, it will be useful to express the angular momentum operators in terms of the base of Table 1. Each matrix matches the representation of the Cartesian components of individual angular momenta in a system of two virtual spin-1/2 nuclei. By a simple calculation, it is shown that

$$\begin{aligned} 2I_z &= 2z_1 + z_2 \\ 2I_x &= \sqrt{3}x_2 + x_1x_2 + y_1y_2 \\ 2I_y &= \sqrt{3}y_2 + y_1x_2 - x_1y_2. \end{aligned} \quad [2]$$

Using these relations, one finds

$$H_Q = \frac{\omega_Q}{2} \sum_k z_{1k} z_{2k}. \quad [3]$$

The formal complexity of the quadrupolar Hamiltonian can be considerably reduced by noting that the expectation value of any observable  $Q$  remains unchanged if all relevant operators are replaced by those obtained after performing a unitary transformation  $U$ , i.e.,

$$\begin{aligned} \langle Q \rangle &= \text{Tr}\{Qe^{-iHt}\sigma e^{iHt}\} \\ &= \text{Tr}\{UQU^\dagger e^{-iUHU^\dagger t}U\sigma U^\dagger e^{iUHU^\dagger t}\}. \end{aligned} \quad [4]$$

From a purely formal point of view, this relation implies that the

**TABLE 1**  
**Matrix Representations of Individual Pauli Operators and Useful Properties**

Pauli operators

$$z_1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}, \quad x_1 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \quad y_1 = \begin{pmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{pmatrix}$$

$$z_2 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}, \quad x_2 = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \quad y_2 = \begin{pmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{pmatrix}$$

Some useful properties

For  $j = 1, 2 \rightarrow [z_j, x_j] = 2iy_j$  and cyclic permutations

For  $k \neq j \rightarrow [z_j, x_k] = 0, [z_j, y_k] = 0, \text{ etc.}$

For  $j = 1, 2 \rightarrow z_j x_j = iy_j$  and cyclic permutations

For  $j = 1, 2 \rightarrow z_j^2 = x_j^2 = y_j^2 = 1$

Finally,  $\text{Tr}\{u_{kl}v_{j'l'}\} = \delta_{uv}\delta_{kj}\delta_{l'l'} \text{Tr}\{1\}$  for  $u, v = x, y, z; k, j = 1, 2; l, l' = 1 \dots N_I$

*Note.*  $N_I$  represents the total number of resonant spins.

real system may be described using a virtual representation in which the Hamiltonian  $H$  and the density matrix  $\sigma$  have been replaced through the correspondence  $H \rightarrow UHU^\dagger$  and  $\sigma \rightarrow U\sigma U^\dagger$ . As will be shown below, the transformation defined by

$$U = U^\dagger = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \quad [5]$$

will be of particular use. After an elementary calculation, the following correspondence is found

$$\begin{aligned} z_1 &\rightarrow z_1 z_2, & z_2 &\rightarrow z_2 \\ x_1 &\rightarrow x_1, & x_2 &\rightarrow x_1 x_2 \\ y_1 &\rightarrow y_1 z_2, & y_2 &\rightarrow x_1 y_2. \end{aligned} \quad [6]$$

According to Eqs. [2] and [3], it follows that

$$\begin{aligned} H_Q &\rightarrow \frac{1}{2}\omega_Q \sum_k z_{1k}, & 2I_{xk} &\rightarrow \sqrt{3}x_{1k}x_{2k} + x_{2k} - z_{1k}x_{2k} \\ 2I_{zk} &\rightarrow 2z_{1k}z_{2k} + z_{2k}, & 2I_{yk} &\rightarrow \sqrt{3}x_{1k}y_{2k} - y_{2k} + z_{1k}y_{2k}. \end{aligned} \quad [7]$$

In this scheme, the quadrupolar Hamiltonian is found to be formally equivalent to a Zeeman Hamiltonian depending on the virtual particle ( $I$ ). Furthermore, since  $z_1$  is a Pauli operator, the level spacing is constant and equal to  $\omega_Q$ . This fact, as shown immediately below, will be of great utility for identifying the secular part of the dipolar Hamiltonian.

(ii) *Dipolar Interaction*

The standard form for the dipolar Hamiltonian is

$$H_D = \frac{1}{2} \sum_{k \neq l} \sum_{q=-2}^2 F_{kl}^{(q)} A_{kl}^{(q)}. \quad [8]$$

The function  $F_{kl}^{(q)}$  describes the orientation and  $A_{kl}^{(q)}$  contains the spin operators:

$$\begin{aligned} A_{kl}^{(0)} &= b_{kl} \left\{ I_{zk} J_{zl} - \frac{1}{4}(I_k^+ J_l^- + I_k^- J_l^+) \right\}, & F_{kl}^{(0)} &= 1 - 3 \cos^2 \theta_{kl} \\ A_{kl}^{(\pm 1)} &= -\frac{3}{2} b_{kl} (I_{zk} J_l^\pm + I_k^\pm J_{zl}), & F_{kl}^{(\pm 1)} &= \sin \theta_{kl} \cos \theta_{kl} e^{\mp i \phi_{kl}} \\ A_{kl}^{(\pm 2)} &= -\frac{3}{4} b_{kl} I_k^\pm J_l^\pm, & F_{kl}^{(\pm 2)} &= \sin^2 \theta_{kl} e^{\mp i 2 \phi_{kl}} \end{aligned}$$

with

$$b_{kl} = \frac{\mu_o \gamma_k \gamma_l \hbar}{4\pi r_{kl}^3}.$$

In the above expression,  $J_l$  represents a neighboring spin pertaining either to the species  $I$  or to a different one,  $\theta_{kl}$  is the angle between the principal direction of the electric field gradient ( $z$  axis) and the internuclear vector  $r_{kl}$ , and  $\phi_{kl}$  is the azimuthal angle with respect to the  $x$  axis.

If, as it will be assumed, the quadrupolar Hamiltonian is dominant, the dipolar interaction represents a perturbation which, as usual, leads to the mixing of the eigenstates of  $H_Q$  and induces transitions which affect the otherwise free time evolution of any generated spin coherence. In a resonance experiment, such transitions promote two kinds of effects: on the one hand, they

**TABLE 2**  
**Relevant Spin Operators in the Dipolar Hamiltonian Expressed as a Function of Spin-1/2 Operators**

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Homonuclear contributions	
$I_{zk} I_{zl} \rightarrow \frac{1}{4}(4z_{1k}z_{1l} + 2z_{1k} + 2z_{1l} + 1)z_{2k}z_{2l}$	
$\frac{1}{4}(I_k^+ I_l^- + I_k^- I_l^+) \rightarrow \frac{1}{4^2} \{ (x_{2k}^+ x_{2l}^- + x_{2k}^- x_{2l}^+) (z_{1k}z_{1l} - z_{1k} - z_{1l} + 1$	
$+ \frac{3}{4}(x_{1k}^+ x_{1l}^- + x_{1k}^- x_{1l}^+) + \frac{3}{4}(x_{1k}^+ x_{1l}^+ + x_{1k}^- x_{1l}^-) \} + \sqrt{3}(x_{2k}^+ x_{2l}^+ + x_{2k}^- x_{2l}^-) (x_{1k}z_{1l} + z_{1k}x_{1l} - x_{1k} - x_{1l}) \}$	
$(I_{zk} I_l^\pm + I_k^\pm I_{zl}) \rightarrow \frac{1}{4} \{ -2(z_{2k}x_{2l}^\mp + x_{2k}^\mp z_{2l})z_{1k}z_{1l} + (2z_{2k}x_{2l}^\mp - x_{2k}^\mp z_{2l})z_{1k}$	
$+ (2x_{2k}^\mp z_{2l} - z_{2k}x_{2l}^\mp)z_{1l} + z_{2k}x_{2l}^\mp + x_{2k}^\mp z_{2l} + 2\sqrt{3}(z_{1k}x_{1l}z_{2k}x_{2l}^\pm + x_{1k}z_{1l}x_{2k}^\pm z_{2l})$	
$+ \sqrt{3}(x_{1l}z_{2k}x_{2l}^\pm + x_{1k}x_{2k}^\pm z_{2l}) \}$	
$I_k^\pm I_l^\pm \rightarrow \frac{1}{4} \{ z_{1k}z_{1l}x_{2k}^\mp x_{2l}^\mp - z_{1k}x_{2k}^\mp x_{2l}^\mp - z_{1l}x_{2k}^\mp x_{2l}^\mp + x_{2k}^\mp x_{2l}^\mp$	
$- \sqrt{3}(z_{1k}x_{1l}x_{2k}^\mp x_{2l}^\pm + x_{1k}z_{1l}x_{2k}^\pm x_{2l}^\mp - x_{1k}x_{2k}^\pm x_{2l}^\mp - x_{1l}x_{2k}^\mp x_{2l}^\pm)$	
$+ \frac{3}{4}x_{2k}^\pm x_{2l}^\pm (x_{1k}^\pm x_{1l}^\mp + x_{1k}^\mp x_{1l}^\pm) + \frac{3}{4}x_{2k}^\pm x_{2l}^\pm (x_{1k}^\pm x_{1l}^\pm + x_{1k}^\mp x_{1l}^\mp) \}$	
Heteronuclear contributions	
$I_{zk} S_{zl} \rightarrow \frac{1}{2}(2z_{1k}z_{2k} + z_{2k})s_{zl}$	
$\frac{1}{4}(I_k^+ S_l^- + I_k^- S_l^+) \rightarrow \frac{1}{8}(-z_{1k}(x_{2k}^+ s_l^+ + x_{2k}^- s_l^-) + (x_{2k}^+ s_l^+ + x_{2k}^- s_l^-) + \sqrt{3}x_{1k}(x_{2k}^+ s_l^- + x_{2k}^- s_l^+))$	
$I_{zk} S_l^\pm + I_k^\pm S_{zl} \rightarrow \frac{1}{2}(z_{1k}(2z_{2k}s_l^\pm - x_{2k}^\mp s_{zl}) + (z_{2k}s_l^\pm + x_{2k}^\mp s_{zl}) + \sqrt{3}x_{1k}x_{2k}^\pm s_{zl})$	
$I_k^\pm S_l^\pm \rightarrow \frac{1}{2}(-z_{1k}x_{2k}^\mp s_l^\pm + x_{2k}^\mp s_l^\pm + \sqrt{3}x_{1k}x_{2k}^\pm s_l^\pm)$	

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*Note.* As in Eq. [7], an arrow has been used to indicate the underlying unitary transformation (see text). On the other hand,  $x^\pm = x \pm iy$ .

give rise to satellite lines (in this case, at  $\omega_D \ll \omega_Q$ ); on the other, they produce a broadening of the main resonance line usually known as ‘‘homogeneous.’’ This broadening arises from transitions between different configurations of the spin ensemble, which, nonetheless, do not alter the energy belonging to the reservoir  $H_Q$ . This condition identifies the matrix elements of  $H_D$ , which, as a whole, give rise to the so-called ‘‘secular’’ part of the dipolar Hamiltonian  $H'_D$ . In the Heisemberg representation, the time derivative of  $H_Q(t) = e^{iHt}H_Q e^{-iHt}$  satisfies the relation

$$\begin{aligned} \frac{d}{dt} H_Q(t) &= -i[H_Q(t), H(t)] \\ &= -ie^{iHt} \{ [H_Q, H'_D] + [H_Q, H''_D] \} e^{-iHt} \quad [9] \end{aligned}$$

from which it is easily inferred that, by definition, the secular dipolar Hamiltonian commutes with  $H_Q$ , i.e.,

$$[H_Q, H'_D] = 0. \quad [10]$$

Giving rise to repeated misinterpretations, this result should be used with care: if any term of the dipolar interaction series (Eq. [8]) does not commute with  $H_Q$ , it can only be stated that its contribution to the nonsecular dipolar Hamiltonian differs from zero. On the other hand, nothing can be said with regard to the secular contribution which, in a second stage, should arise from a careful analysis of all matrix elements. The situation is simple in nuclear magnetic resonance where, as a result of the particular  $I_z$  dependence of the (dominant Zeeman) Hamiltonian, all terms in  $H_D$  (Eq. [8]) which do not commute with  $H_Z$  can be disregarded as entirely nonsecular. This result should, however, be extended

to nuclear quadrupole resonance if all homo- and heteronuclear dipolar interactions are represented by means of the previous section formalism. A list containing all dipolar terms in Eq. [8] expressed as a combination of (transformed) 1/2 spin operators has been included in Table 2: all secular as well as nonsecular contributions to  $H_Q$  can be easily detected.

As a useful example for understanding the origin of secular parts in quadrupolar resonance, terms like  $F_{kl}^{(\pm 2)} I_k^\pm I_l^\pm$  in Eq. [8] should be considered: matrix elements different from zero link two spin states  $(\pm 3/2, \pm 3/2) \leftrightarrow (\pm 1/2, \pm 1/2)$ ,  $(\pm 3/2, \pm 1/2) \leftrightarrow (\pm 1/2, \mp 1/2)$ ,  $(\pm 1/2, \pm 3/2) \leftrightarrow (\mp 1/2, \pm 1/2)$ ,  $(\pm 3/2, \mp 1/2) \leftrightarrow (\pm 1/2, \mp 3/2)$ , and  $(\pm 1/2, \pm 1/2) \leftrightarrow (\mp 1/2, \mp 1/2)$ . Due to the inherent degeneracy of  $H_Q$ , dipolar transitions between  $(\pm 3/2, \mp 1/2) \leftrightarrow (\pm 1/2, \mp 3/2)$  and  $(\pm 1/2, \pm 1/2) \leftrightarrow (\mp 1/2, \mp 1/2)$  do not alter the quadrupolar Hamiltonian energy and, by this means, lead to secular contributions in  $H'_D$  (represented by those terms commuting with  $z_1 \equiv \sum z_{1k}$  in Table 2). As a final remark, it is worth noting that the operator  $I_k^+ I_l^- + I_k^- I_l^+$  is not completely secular<sup>2</sup> since  $[I_k^+ I_l^- + I_k^- I_l^+, H_Q] \neq 0$ .

After disregarding nonsecular terms, it results that

$$\begin{aligned} H_D'' &\rightarrow \frac{1}{2} \sum_{k \neq l} \{ h_{kl}^{(1)} z_{1k} z_{1l} + h_{kl}^{(2)} (x_{1k}^+ x_{1l}^- + x_{1k}^- x_{1l}^+) \\ &\quad + 2h_{kl}^{(3)} z_{1k} + h_{kl}^{(4)} \}, \quad [11] \end{aligned}$$

<sup>2</sup> Flip-flop transitions like  $(\pm 1/2, \pm 1/2) \leftrightarrow (\pm 3/2, \mp 1/2)$  do alter the quadrupolar energy.

where

$$\begin{aligned}
h_{kl}^{(1)} &= \frac{b_{kl}}{4} \left\{ F_{kl}^{(0)} \left( 4z_{2k}z_{2l} - \frac{1}{4}(x_{2k}^+x_{2l}^- + x_{2k}^-x_{2l}^+) \right) \right. \\
&\quad + 3F_{kl}^{(1)}(z_{2k}x_{2l}^- + x_{2k}^-z_{2l}) + 3F_{kl}^{(-1)}(z_{2k}x_{2l}^+ + x_{2k}^+z_{2l}) \\
&\quad \left. - \frac{3}{4}F_{kl}^{(2)}x_{2k}^-x_{2l}^- - \frac{3}{4}F_{kl}^{(-2)}x_{2k}^+x_{2l}^+ \right\} \\
h_{kl}^{(2)} &= \frac{3}{4} \frac{b_{kl}}{4} \left\{ -\frac{F_{kl}^{(0)}}{4}(x_{2k}^+x_{2l}^- + x_{2k}^-x_{2l}^+) - \frac{3}{4}F_{kl}^{(2)}x_{2k}^+x_{2l}^+ \right. \\
&\quad \left. - \frac{3}{4}F_{kl}^{(-2)}x_{2k}^-x_{2l}^- \right\} \\
h_{kl}^{(3)} &= \frac{b_{kl}}{4} \left\{ F_{kl}^{(0)} \left( 2z_{2k}z_{2l} + \frac{1}{4}(x_{2k}^+x_{2l}^- + x_{2k}^-x_{2l}^+) \right) \right. \\
&\quad - \frac{3}{2}F_{kl}^{(1)}(2z_{2k}x_{2l}^- - x_{2k}^-z_{2l}) - \frac{3}{2}F_{kl}^{(-1)}(2z_{2k}x_{2l}^+ - x_{2k}^+z_{2l}) \\
&\quad \left. + \frac{3}{4}F_{kl}^{(2)}x_{2k}^-x_{2l}^- + \frac{3}{4}F_{kl}^{(-2)}x_{2k}^+x_{2l}^+ \right\} \\
h_{kl}^{(4)} &= \frac{b_{kl}}{4} \left\{ F_{kl}^{(0)} \left( z_{2k}z_{2l} - \frac{1}{4}(x_{2k}^+x_{2l}^- + x_{2k}^-x_{2l}^+) \right) \right. \\
&\quad - \frac{3}{2}F_{kl}^{(1)}(z_{2k}x_{2l}^- + x_{2k}^-z_{2l}) - \frac{3}{2}F_{kl}^{(-1)}(z_{2k}x_{2l}^+ + x_{2k}^+z_{2l}) \\
&\quad \left. - \frac{3}{4}F_{kl}^{(2)}x_{2k}^-x_{2l}^- - \frac{3}{4}F_{kl}^{(-2)}x_{2k}^+x_{2l}^+ \right\}.
\end{aligned}$$

Contributions due to unlike spins (without quadrupolar couplings) give rise to the heteronuclear part

$$H_D^{HS} \rightarrow \sum_{k,l} \{g_{kl}^{(1)}z_{1k} + g_{kl}^{(2)}\} \quad [12]$$

with

$$\begin{aligned}
g_{kl}^{(1)} &= \frac{b_{kl}}{2} \left\{ F_{kl}^{(0)} \left( 2z_{2k}s_{zl} + \frac{1}{4}(x_{2k}^+s_l^+ + x_{2k}^-s_l^-) \right) \right. \\
&\quad - \frac{3}{2}F_{kl}^{(1)}(2z_{2k}s_l^+ - x_{2k}^-s_{lz}) - \frac{3}{2}F_{kl}^{(-1)}(2z_{2k}s_l^- - x_{2k}^+s_{lz}) \\
&\quad \left. + \frac{3}{4}F_{kl}^{(2)}x_{2k}^-s_l^+ + \frac{3}{4}F_{kl}^{(-2)}x_{2k}^+s_l^- \right\} \\
g_{kl}^{(2)} &= \frac{b_{kl}}{2} \left\{ F_{kl}^{(0)} \left( z_{2k}s_{zl} - \frac{1}{4}(x_{2k}^+s_l^+ + x_{2k}^-s_l^-) \right) \right. \\
&\quad - \frac{3}{2}F_{kl}^{(1)}(z_{2k}s_l^+ + x_{2k}^-s_{lz}) - \frac{3}{2}F_{kl}^{(-1)}(z_{2k}s_l^- + x_{2k}^+s_{lz}) \\
&\quad \left. - \frac{3}{4}F_{kl}^{(2)}x_{2k}^-s_l^+ - \frac{3}{4}F_{kl}^{(-2)}x_{2k}^+s_l^- \right\},
\end{aligned}$$

the index  $k(l)$  running over the (non)resonant spins.

(iii) *rf Field: Rotating Frame*

The presence of a radiofrequency radiation field is formally described through the Hamiltonian  $H_{rf} = 2\omega_Q I_X \cos \omega t$  which, in the above formalism, should be expressed by the relation

$$\begin{aligned}
H_{rf} &= 2\omega_1(pI_x + qI_y + rI_z) \cos \omega t \\
&\rightarrow \omega_1 \sum_k (\sqrt{3}x_{1k}(px_{2k} + qy_{2k})) \\
&\quad + z_{1k}(2rz_{2k} + qy_{2k} - px_{2k}) \\
&\quad + (rz_{2k} - qy_{2k} + px_{2k}) \cos \omega t, \quad [13]
\end{aligned}$$

with  $p, q$ , and  $r$  representing the direction cosines of the coil axis  $X$  with respect to the crystalline reference frame. The evolution of the density matrix  $\sigma$  in the presence of rf irradiation is usually described through the use of an interaction representation by defining  $(I) \sigma^* = \exp(i\omega t \sum (z_{1k}z_{2k})/2) \sigma \exp(-i\omega t \sum (z_{1k}z_{2k})/2)$ . Using the present formalism  $\sigma^*$  becomes  $\sigma^* \rightarrow \exp(i\omega z_{1t}/2) U \sigma U^\dagger \exp(-i\omega z_{1t}/2)$  which, in turn, corresponds to the standard NMR “rotating-frame” picture. Now, assuming that all operators have been conveniently transformed, the following equation holds,

$$\frac{d\sigma^*}{dt} = -i \left[ H^* - \frac{z_1\omega}{2}, \sigma^* \right] = -i [H_D' + H_{rf}^*, \sigma^*], \quad [14]$$

where, for simplicity's sake, the rf irradiation has been assumed to be resonant. By this procedure, the rf Hamiltonian  $H_{rf}^*$  takes on the form

$$\begin{aligned}
H_{rf}^* &\rightarrow \omega_1 \sum_k \left( \frac{\sqrt{3}}{2} \lambda x_{1k} x'_{2k} (1 + \cos 2\omega t) \right. \\
&\quad + \frac{\sqrt{3}}{2} \lambda y_{1k} x'_{2k} \sin 2\omega t \\
&\quad \left. + \gamma z_{1k} z'_{2k} \cos \omega t + z''_{2k} \cos \omega t \right), \quad [15]
\end{aligned}$$

where

$$\begin{aligned}
x'_{2k} &= \frac{1}{\lambda} (px_{2k} + qy_{2k}); & \lambda^2 &= p^2 + q^2 \\
z'_{2k} &= \frac{1}{\gamma} (2rz_{2k} - px_{2k} + qy_{2k}); & \gamma^2 &= (2r)^2 + p^2 + q^2 \\
z''_{2k} &= rz_{2k} + px_{2k} - qy_{2k}.
\end{aligned}$$

In the rotating reference frame, those terms varying with frequency  $\omega$  and  $2\omega$  do not induce appreciable effects and, for this reason, only time-independent contributions in  $H_{rf}^*$  should be retained. Furthermore, since the electric field gradient at the nucleus site has been assumed to be axially symmetric, the reference system may be chosen in a way that  $q = 0$  and  $p \neq 0$ . It

**TABLE 3**  
**Laboratory- and Rotating-Frame Representations of Different rf Hamiltonians in a Crossed Coil System**

Coil	$p$	$q$	$H_{rf}$	$H_{rf}^* \rightarrow$
1	$\neq 0$	0	$2\omega_1 \cos \omega t \sum_k I_{xk}$	$\frac{\sqrt{3}}{2} p \omega_1 \sum_k x_{1k} x_{2k}$
1	$\neq 0$	0	$2\omega_1 \sin \omega t \sum_k I_{yk}$	$\frac{\sqrt{3}}{2} p \omega_1 \sum_k y_{1k} x_{2k}$
2	0	$\neq 0$	$2\omega_1 \cos \omega t \sum_k I_{yk}$	$\frac{\sqrt{3}}{2} q \omega_1 \sum_k x_{1k} y_{2k}$
2	0	$\neq 0$	$2\omega_1 \sin \omega t \sum_k I_{yk}$	$\frac{\sqrt{3}}{2} q \omega_1 \sum_k y_{1k} y_{2k}$

then follows that

$$H_{rf}^* \rightarrow \frac{\sqrt{3}}{2} \omega_1 p \sum_k x_{1k} x_{2k}. \quad [16]$$

It is important to note that, even in the case  $\lambda = 1$  (principal direction of the field gradient perpendicular to the coil axis), a  $90^\circ$  phase-shifted rf pulse is physically different from that obtained by means of a second coil perpendicular to the first one and irradiating in phase ( $p' = 0, q' = 1$ ). This situation markedly contrasts with that found in nuclear magnetic resonance and could be used for eventual applications: differences are just formal if one applies a unique pulse to a sample in thermal equilibrium but a second coil could be useful when dealing with coherences created after the first pulse. A list containing four different operators related to either the first or the second coil and under different phase conditions has been included in Table 3. It is worth mentioning that, in the more general situation  $0 < \lambda < 1$ , a similar ‘‘angular rotation’’ in both coils could be obtained by independently adjusting the rf field amplitude until getting  $p\omega_1 = q'\omega_1'$ . Furthermore, a simultaneous irradiation allows the combination of phases and amplitudes so as to change at will the ‘‘rotation axis’’ for operators only depending on one virtual particle. At least in part, these concepts will be used in the next section when the polarization evolution during a pulse sequence is described.

#### (iv) Polarization during a Two-Pulse Sequence: Echo Signal

If, maintaining calculations as simple as possible, the coil axis is oriented so as to obtain  $\lambda = p = 1$ , the resonance signal following a rf- $\tau$ -rf pulse sequence should be proportional to

$$\langle I_x \rangle(t) = \text{Tr}\{I_x^* \sigma^*(t)\}, \quad [17]$$

where

$$\begin{aligned} \sigma^*(t) &= e^{-iH_b t'} \text{Re}^{-iH_b \tau} \sigma^*(0_+) e^{iH_b \tau} R^\dagger e^{iH_b t'} \rightarrow U \sigma^*(t) U^\dagger \\ I_x^* &= e^{i\frac{\omega_Q}{2} z_1 z_2 t} I_x e^{-i\frac{\omega_Q}{2} z_1 z_2 t} \rightarrow \frac{1}{2} (\sqrt{3} x_1 x_2 \cos \omega_Q t \\ &\quad - \sqrt{3} y_1 x_2 \sin \omega_Q t + x_2 - z_1 x_2). \end{aligned}$$

In the above expression,  $\sigma^*(0_+)$  represents the density matrix immediately after the first pulse and  $t' = t - \tau$  indicates the elapsed time since the second rf pulse  $R$  is applied; for brevity's sake, it has been written  $z_1 z_2 \equiv \sum z_{1k} z_{2k}$ ,  $y_1 x_2 \equiv \sum y_{1k} x_{2k}$ , etc. If the time separation between pulses is short enough, a power series expansion enables  $\sigma^*(t)$  to be rewritten as

$$\begin{aligned} \sigma^*(t) &= \left\{ \hat{\sigma}(0_+) - it' [H'_D, \hat{\sigma}(0_+)] - i\tau [\hat{H}'_D, \hat{\sigma}(0_+)] \right. \\ &\quad - \frac{t'^2}{2} [H'_D, [H'_D, \hat{\sigma}(0_+)]] - \frac{\tau^2}{2} [\hat{H}'_D, [\hat{H}'_D, \hat{\sigma}(0_+)]] \\ &\quad \left. - t'\tau [H'_D, [\hat{H}'_D, \hat{\sigma}(0_+)]] + \dots \right\} \quad [18] \end{aligned}$$

with  $\hat{\sigma} = R \sigma^* R^\dagger$  and  $\hat{H}'_D = R H'_D R^\dagger$ . Assuming that before the first pulse is applied the system is in thermal equilibrium, we write, as a shorthand notation,

$$\sigma_{eq} \rightarrow z_1. \quad [19]$$

After a  $(\pi/2)_0$  pulse, the density matrix takes on the form

$$\sigma(0_+) \rightarrow e^{-i\frac{\pi}{4} x_1 x_2} z_1 e^{i\frac{\pi}{4} x_1 x_2} = -y_1 x_2, \quad [20]$$

where, as usual, the condition  $\omega_1 \gg H_D$  has been assumed to hold. After combining expressions [17], [18], and [20], one obtains

$$\begin{aligned} \langle I_x \rangle(t) &\cong \sin(\omega_Q t) \text{Tr}\{y_1 x_2 y_1 \hat{x}_2 - it' H'_D [y_1 \hat{x}_2, y_1 x_2] \\ &\quad - i\tau \hat{H}'_D [y_1 \hat{x}_2, y_1 x_2] - \frac{t'^2}{2} [H'_D, [H'_D, y_1 \hat{x}_2]] y_1 x_2 \\ &\quad - \frac{\tau^2}{2} [H'_D, [H'_D, y_1 x_2]] y_1 \hat{x}_2 \\ &\quad - t'\tau [H'_D, [\hat{H}'_D, y_1 \hat{x}_2]] y_1 x_2\}, \quad [21] \end{aligned}$$

where, as a brief notation, it has been defined  $y_1 \hat{x}_2 = R y_1 x_2 R^\dagger$ ,  $y_1 \check{x}_2 = R^\dagger y_1 x_2 R$ , and  $H'_D$  represents the transformed dipolar Hamiltonian (Eqs. [11] and [12]). Formula [21] describes in a general manner the ‘‘in-phase’’ contribution to the resonance signal. Further features of the nuclear response should be obtained after defining the phase and length of the second pulse  $R$ . Immediately below, two of the most popular echo pulse sequences will be studied in detail.

*Case I: Hahn-echo sequence*  $((\pi/2)_{0-\tau} - (\pi)_{0-\tau})$ . In this case,  $R = \exp(-i\pi x_1 x_2/2)$ , so that

$$\begin{aligned} \langle I_x \rangle_{HE}(t) &= -\sin(\omega_Q t) \text{Tr} \left\{ (y_1 x_2)^2 + \frac{(t'^2 + \tau^2)}{2} [H'_D, y_1 x_2]^2 \right. \\ &\quad \left. - t'\tau [H'_D, y_1 x_2] R [H'_D, y_1 x_2] R^\dagger \right\}. \quad [22] \end{aligned}$$

A complete expression for  $[H'_D, y_1 x_2]$  has been included in

**TABLE 4**  
**Complete Expressions for the Homo- and Heteronuclear Part of the Conmutator  $[H'_D, \Sigma_{y1j} x_{2j}]$**

Homonuclear part

$$\begin{aligned} [H'_D, \Sigma_j y_{1j} x_{2j}] = & \sum_{k \neq l} \{ (A_{kl} + C_{kl}) x_{1k} z_{1l} x_{2l} + (A_{kl} - C_{kl}) y_{1k} z_{2k} y_{2l} \\ & + \frac{3}{2} (A_{kl} - C_{kl} + \frac{4}{3} A_{kl}) y_{1k} y_{2k} z_{2l} - \frac{3}{2} (A_{kl} + C_{kl}) z_{1k} x_{1l} x_{2l} + 2 B_{kl} z_{1k} x_{2k} y_{1l} y_{2l} \\ & - 2 B_{kl} x_{1k} z_{2l} + 2 B'_{kl} y_{1k} y_{2k} y_{2l} - 2 B'_{kl} y_{1k} z_{2k} z_{2l} + C'_{kl} x_{1k} y_{2l} + C'_{kl} z_{1k} x_{2k} y_{1l} z_{2l} \\ & + \sum_{k \neq l} \{ 4 A_{kl} z_{1k} z_{2k} y_{1l} y_{2l} - (A_{kl} + C_{kl}) x_{1k} x_{2l} - (A_{kl} - C_{kl}) z_{1k} y_{2k} y_{1l} z_{2l} \\ & - 4 B_{kl} x_{1k} z_{1l} z_{2l} - 2 B_{kl} y_{1k} y_{2k} x_{2l} - 2 B'_{kl} z_{1k} y_{2k} y_{1l} y_{2l} - 4 B'_{kl} z_{1k} z_{2k} y_{1l} z_{2l} \\ & - C'_{kl} y_{1k} z_{2k} x_{2l} - C'_{kl} x_{1k} z_{1l} y_{2l} + \frac{3}{2} C'_{kl} z_{2k} y_{1l} x_{2l} - \frac{3}{2} C'_{kl} z_{1k} x_{1l} y_{2l} \} \end{aligned}$$

where

$$\begin{aligned} A_{kl} &= \left(\frac{ib_{kl}}{4}\right) F_{kl}^{(0)} \\ B_{kl} &= \left(\frac{ib_{kl}}{4}\right) \left(\frac{3}{2}\right) (F_{kl}^{(1)} + F_{kl}^{(-1)}), & B'_{kl} &= \left(\frac{ib_{kl}}{4}\right) \left(\frac{3i}{2}\right) (F_{kl}^{(1)} - F_{kl}^{(-1)}) \\ C_{kl} &= \left(\frac{ib_{kl}}{4}\right) \left(\frac{3}{2}\right) (F_{kl}^{(2)} + F_{kl}^{(-2)}), & C'_{kl} &= \left(\frac{ib_{kl}}{4}\right) \left(\frac{3i}{2}\right) (F_{kl}^{(2)} - F_{kl}^{(-2)}) \end{aligned}$$

Heteronuclear part

$$[H'_D, y_{1x_2}] = 2i \sum_{k,l} (\tilde{A}_{kl} y_{1k} y_{2k} - \tilde{B}_{kl} x_{1k} + \tilde{C}_{kl} y_{1k} z_{2k})$$

where

$$\begin{aligned} \tilde{A}_{kl} &= \frac{b_{kl}}{2} \{ F_{kl}^{(0)} s_{z_l} - \frac{3}{2} (F_{kl}^{(1)} + F_{kl}^{(-1)}) s_{x_l} - \frac{3i}{2} (F_{kl}^{(1)} - F_{kl}^{(-1)}) s_{y_l} \} \\ \tilde{B}_{kl} &= \frac{b_{kl}}{2} \{ \frac{F_{kl}^{(0)}}{2} s_{x_l} + \frac{3}{2} (F_{kl}^{(1)} + F_{kl}^{(-1)}) s_{z_l} + \frac{3}{4} (F_{kl}^{(2)} + F_{kl}^{(-2)}) s_{x_l} + \frac{3i}{4} (F_{kl}^{(2)} - F_{kl}^{(-2)}) s_{y_l} \} \\ \tilde{C}_{kl} &= \frac{b_{kl}}{2} \{ -\frac{F_{kl}^{(0)}}{2} s_{y_l} - \frac{3i}{2} (F_{kl}^{(1)} - F_{kl}^{(-1)}) s_{z_l} + \frac{3}{4} (F_{kl}^{(2)} + F_{kl}^{(-2)}) s_{y_l} - \frac{3i}{4} (F_{kl}^{(2)} - F_{kl}^{(-2)}) s_{x_l} \} \end{aligned}$$

Table 4. Although the calculations in Eq. [22] seem to be extremely complex, crossed contributions to the trace coming from products of different terms  $T_{lD}, T'_{lD}$  in  $H'_D$  are always zero. This fact immediately leads to the relation

$$R[T_{lD}, y_{1x_2}]R^\dagger = [T_{lD}, y_{1x_2}] \quad [23]$$

as a condition for independently recognizing those contributions to  $H'_D$  which are refocused at  $t' = \tau$ . According to these results, it is not difficult to show that the conmutator  $[H'^{IS}_D, y_{1x_2}]$  satisfies Eq. [23] and, from this, it follows that the Hahn sequence refocuses the whole heteronuclear dipolar contribution.<sup>3</sup>

To a certain extent, this result should be a surprise: in striking contrast with magnetic resonance, interactions due to nuclei having a different spin  $S$  give rise to contributions which cannot be visualized as simple “field inhomogeneities” ( $kI_z S_z$ -type contributions) and which, as a consequence, are not inverted after a  $\pi$  pulse. In fact, it is worth noting that (see Table 4 for notation)

$$\begin{aligned} RH'^{IS}_D R^\dagger &= R \sum_{k,l} (2\tilde{A}_{kl} z_{1k} z_{2k} + \tilde{B}_{kl} z_{1k} x_{2k} + \tilde{C}_{kl} z_{1k} y_{2k} \\ &+ \tilde{A}_{kl} z_{2k} - \tilde{B}_{kl} x_{2k} - \tilde{C}_{kl} y_{2k}) R^\dagger \end{aligned}$$

<sup>3</sup> A similar reasoning shows that, with the exception of an echo sign change, an identical result is obtained with the alternative pulse sequence  $(\pi/2)_{0-\tau} - (\pi)_{90-\tau}$ .

$$\begin{aligned} &= \sum_{k,l} (2\tilde{A}_{kl} z_{1k} z_{2k} - \tilde{B}_{kl} z_{1k} x_{2k} + \tilde{C}_{kl} z_{1k} y_{2k} \\ &- \tilde{A}_{kl} z_{2k} - \tilde{B}_{kl} x_{2k} + \tilde{C}_{kl} y_{2k}) \neq -H'^{IS}_D \quad [24] \end{aligned}$$

even though no heteronuclear contribution affects (to second order) the echo amplitude at  $t' = \tau$ . Differences between the NQR and the NMR cases are stressed if, as an alternative path,  $R$  indicates a  $90^\circ$  phase-shifted  $\pi$  pulse coming from a  $90^\circ$  rotated second coil (see Section (iii)). Although no consequences are expected in an NMR Hahn-type sequence, the situation is rather different in a quadrupole resonance experiment: in this case,  $R = \exp(-i\pi y_1 y_2 / 2)$  and since  $R y_1 x_2 R^\dagger = -y_1 x_2$ , Eqs. [22] and [23] hold. On the other hand

$$R[H'^{IS}_D, y_{1x_2}]R^\dagger = 2i \sum_{k,l} (\tilde{A}_{kl} y_{1k} y_{2k} + \tilde{B}_{kl} x_{1k} - \tilde{C}_{kl} y_{1k} z_{2k}), \quad [25]$$

leading to only a partial elimination of heteronuclear interactions.

Special attention will now be paid to the homonuclear part of the conmutator  $[H'_D, y_{1x_2}]$  which, for convenience, has been expressed in Table 4 as a superposition of two contributions with complementary properties: after a  $(\pi)_0$  pulse is applied, terms enclosed within the second summation remain unchanged and, according to formula [23], lead to a homonuclear Hahn echo at

$t' = \tau$ . This implies that the gradual echo decay as  $\tau$  rises is due to only a fraction of the homonuclear dipolar Hamiltonian, a result which, once again, contrasts with that holding in magnetic resonance.

The results obtained for homo- and heteronuclear contributions may be summarized by writing the average nuclear polarization as

$$\langle I_x \rangle_{HE} \propto -\sin(\omega_Q t) \left\{ 1 - \frac{1}{2} M_2^{II}(t' + \tau)^2 - \frac{1}{2} (M_2^{III} + M_2^{IS})(t' - \tau)^2 + \dots \right\}. \quad [26]$$

In this expression,  $M_2^{II}$  ( $M_2^{III}$ ) represents the homonuclear component to the second moment due to terms of  $[H_D^{II}, y_1 x_2]$  which do (not) satisfy Eq. [23]. Since squares of spin-1/2 operators are proportional to the identity matrix, explicit expressions for each factor in the above series may be obtained from Eq. [22] by rather simple calculations. After some algebra, one gets

$$M_2^{II} = \frac{1}{N_I} \sum_{k \neq l} \frac{b_{kl}^2}{32} \left\{ 33(1 - 3\gamma_{kl}^2)^2 + 144\gamma_{kl}^2(1 - \gamma_{kl}^2) + 36(1 - \gamma_{kl}^2)^2 + 81(\alpha_{kl}^2 - \beta_{kl}^2)^2 - 36(1 - 3\gamma_{kl}^2)(\alpha_{kl}^2 - \beta_{kl}^2) \right\} \quad [27]$$

$$M_2^{III} = \frac{1}{N_I} \sum_{k \neq l} \frac{b_{kl}^2}{32} \left\{ 36(1 - 3\gamma_{kl}^2)^2 + 360\gamma_{kl}^2(1 - \gamma_{kl}^2) + 36(1 - \gamma_{kl}^2)^2 + 324\alpha_{kl}^2\beta_{kl}^2 \right\},$$

where  $\alpha_{kl} = \sin \theta_{kl} \cos \phi_{kl}$ ,  $\beta_{kl} = \sin \theta_{kl} \sin \phi_{kl}$ , and  $\gamma_{kl} = \cos \theta_{kl}$  are the direction cosines of the internuclear vector. It is worth noting that

$$M_2^{II} = M_2^{III} + M_2^{IS} = \frac{1}{N_I} \sum_{k \neq l} \frac{b_{kl}^2}{32} \left\{ 69(1 - 3\gamma_{kl}^2)^2 + 504\gamma_{kl}^2(1 - \gamma_{kl}^2) + 153(1 - \gamma_{kl}^2)^2 - 36(1 - 3\gamma_{kl}^2)(\alpha_{kl}^2 - \beta_{kl}^2) \right\} \quad [28]$$

in complete agreement with the result obtained by Abragam and Kambe (4) by means of an explicit matrix representation of spin-3/2 operators. Also in accordance is the heteronuclear contribution, which results<sup>4</sup>

$$M_2^{IS} = \frac{1}{N_I} S(S+1) \sum_{\substack{k \text{ over } I \\ l \text{ over } S}} b_{kl}^2 \left\{ \frac{1}{2}(1 - 3\gamma_{kl}^2)^2 + 6\gamma_{kl}^2(1 - \gamma_{kl}^2) + \frac{3}{2}(1 - \gamma_{kl}^2)^2 \right\}. \quad [29]$$

<sup>4</sup> Factor 3 in the last term of Eq. [12] in Ref. (4) probably comes from a typing mistake.

*Case II: Solid-echo sequence*  $((\pi/2)_{0-\tau} - (\pi/2)_{90-\tau})$ . Originally designed for refocusing the homonuclear part of the (secular) dipolar Hamiltonian in the presence of a high magnetic field (5), the NQR sequence induces partially different effects. In the formalism discussed, the second pulse should be represented as

$$R = e^{-i\frac{\pi}{4}y_1x_2} \quad [30]$$

and, consequently,

$$y\hat{x}_2 = y\check{x}_2 = y_1x_2. \quad [31]$$

After replacing in Eq. [21], the following is found for the solid-echo sequence:

$$\langle I_x \rangle_{SE}(t) \cong \sin(\omega_Q t) \text{Tr} \left\{ (y_1x_2)^2 + \frac{(t'^2 + \tau^2)}{2} [H_D', y_1x_2]^2 + t'\tau [H_D', y_1x_2] R [H_D', y_1x_2] R^\dagger \right\}. \quad [32]$$

This expression leads now to the relation

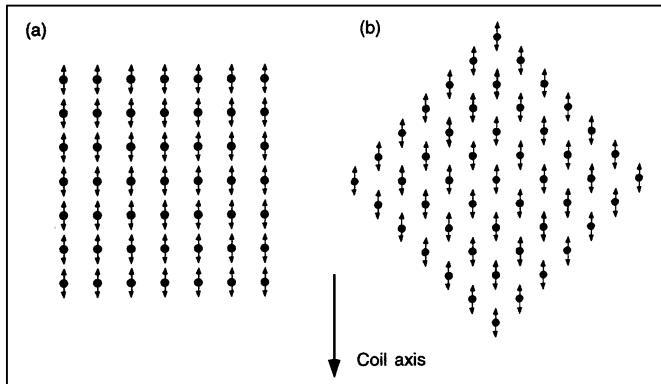
$$R [T_{ID}, y_1x_2] R^\dagger = -[T_{ID}, y_1x_2] \quad [33]$$

for easily detecting refocused contributions  $T_{ID}$  in  $H_D'$ . After a careful examination, it is found that, contrasting with Case I, a complementary fraction of the homonuclear part is now refocused by the solid-echo sequence (first summation in Table 4). A tedious but straightforward calculation leads in this case to the formula

$$\langle I_x \rangle_{SE} \propto \sin(\omega_Q t) \left\{ 1 - \frac{1}{2} M_2^{III}(t' - \tau)^2 - \frac{1}{2} (M_2^{III} + M_2^{IS})(t'^2 + \tau^2) + \dots \right\}, \quad [34]$$

where  $M_2^{II}$ ,  $M_2^{III}$ , and  $M_2^{IS}$  have the same meaning as in Eq. [26]. As found in magnetic resonance, Eqs. [26] and [34] provide complementary experimental information although, in this case, homo- and heteronuclear contributions to the second moment cannot be independently determined, at least by means of only these two sequences. At first sight, the high complexity of the homonuclear dipolar Hamiltonian (Eq. [11]) makes it a rather difficult task to decide whether a different set of pulse sequences exhibiting a better performance could be found. However, this topic deserves a careful examination and will probably be the subject of a future study.

As a final remark, it should be pointed out that, as inferred from Eq. [28], the contribution to the homonuclear second moment due to an arbitrary pair of identical nuclei depends on the azimuthal angle  $\phi$  between the internuclear vector and the coil axis. In other words, the resonance linewidth of a single-crystal sample depends on its relative orientation to the coil axis, even



**FIG. 1.** (a) Virtual single-crystalline sample during an NQR experiment. After an rf pulse, the nuclear polarization oscillates along the coil axis direction. (b) Mutual dipolar interactions are slightly different if the sample is rotated.

if it is assumed (as in this study) that the electric field gradient at the nuclear site is axially symmetric. This fact simply stresses the tensorial nature of quadrupolar interactions and, in this sense, pictures in Fig. 1 may serve as a helpful guide. Contrasting with the magnetic resonance situation, the nuclear polarization following an rf excitation pulse does not precess around the principal direction of the electric field gradient ( $z$  axis) but it rather oscillates ( $\phi$ ) along a direction parallel to the coil axis ( $x$  axis). A rotation of the crystal around  $z$  therefore alters the mutual nuclear induction during the normal evolution of the spin po-

larization and, consequently, modifies the resonance linewidth (see Fig. 1). However, this effect should hardly ever be detected: the contribution to the second moment due to the  $\phi$ -dependent part (last term in Eq. [28]) is not greater than 10%. Due to the presence of uncompensated contributions, this proportion considerably increases if active moments for each pulse sequence are separately analyzed (Eq. [27]). Even in this case, the great variety of pairs of atoms to be considered in a crystal allows one to estimate that, on average, linewidth variations remain outside observation, at least for standard systems.

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