Some Calculations for NQR of Spin 1 Nuclei in Powders
(without using effective spin ½ operators)

Feb 2000
Last updated July 2005

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I. Basic Equations

In the principal axes system, one has a quadrupole Hamiltonian

\[ H_Q = \frac{e^2 q Q}{4 I (2I - 1)} \left[ \left( 3I_z^2 - I^2 \right) + \frac{\eta}{2} \left( I_x^2 + I_y^2 \right) \right] \]  

(1)

For \( I = 1 \) and using the eigenfunctions of \( I_z \), that is \( |+1\rangle, |0\rangle, \text{ and } |-1\rangle \) for a basis one has

\[ H_Q = \frac{e^2 q Q}{4} \begin{pmatrix} 1 & 0 & \eta \\ 0 & -2 & 0 \\ \eta & 0 & 1 \end{pmatrix} \]  

(2)

which has eigenenergies of

\[ \varepsilon_\pm = \left( 1 \pm \frac{\eta}{2} \right) \frac{e^2 q Q}{4} \quad \text{and} \quad \varepsilon_0 = -\frac{2 e^2 q Q}{4} \]  

(3)

and corresponding eigenfunctions

\[ |+\rangle = \frac{1}{\sqrt{2}} \left( |+1\rangle + |-1\rangle \right), \quad |\rangle \equiv \frac{1}{\sqrt{2}} \left( |+1\rangle - |-1\rangle \right), \quad \text{and} \quad |0\rangle \equiv |0\rangle \]  

(4)

The transition frequencies are

\[ \omega_\pm = \left( 1 \pm \frac{\eta}{3} \right) \omega_Q \quad \text{and} \quad \omega_0 = \frac{2}{3} \eta \omega_Q \]  

where

\[ \omega_Q = \frac{3 e^2 q Q}{4 \hbar} \]  

(5)

II. Single Frequency Experiments

A. Linear Polarization

Now apply an RF pulse in the laboratory reference frame, \((x', y', z')\), using an RF coil which
produces a magnetic field of magnitude $B_1$ along $x'$, with an interaction described by the Hamiltonian

$$H_1 = -\gamma_1 \hbar B_1 I_x' \cos(\omega t)$$

(6)

where $\gamma_1$ is the gyromagnetic ratio for the spin-1 nucleus, and

$$I_x = \cos \theta I_z + \sin \theta \cos \phi I_x + \sin \theta \sin \phi I_y$$

$$= \cos \theta I_z + \sin \theta \left(e^{-it} I_+ + e^{it} I_- \right)$$

(7)

If we assume $0 < \xi < 1$, to avoid the complications of degenerate levels and degenerate transition frequencies, and excite only one transition at a time, then by examining the matrix elements for the various operators, one has an effective $H_1$ for each transition given by

$$\omega_+ \rightarrow H_{1\text{eff}} = -\gamma_1 \hbar B_1 \sin \theta \cos \phi I_x$$

$$\omega_- \rightarrow H_{1\text{eff}} = -\gamma_1 \hbar B_1 \sin \theta \sin \phi I_y$$

$$\omega_0 \rightarrow H_{1\text{eff}} = -\gamma_1 \hbar B_1 \cos \theta I_z$$

(8)

Now note that, for example, $\sin \theta \cos \phi$ is the projection of a unit vector along $(\theta, \phi)$ onto the $x$-axis, etc., so with $\alpha$ the angle between $B_1$ and the $y$-axis, and $\beta$ the angle between $B_1$ and the $x$-axis one has

$$\cos \beta = \sin \theta \cos \phi$$

$$\cos \alpha = \sin \theta \sin \phi$$

(9)

Of course $\theta$ is the angle between $B_1$ and the $z$-axis.

Schrödinger’s equation for the evolution of a wavefunction $|\psi\rangle$ is

$$-\frac{\hbar}{i} \frac{\partial \psi}{\partial t} = H\psi$$

(10)

and here we have

$$H = H_0 + H_{1\text{eff}}$$

(11)

and quite generally we can write

$$|\psi(t)\rangle = a(t)|+\rangle \, e^{-i\xi_+ t \hbar} + b(t)|-\rangle \, e^{-i\xi_- t \hbar} + c(t)|0\rangle \, e^{-i\xi_0 t \hbar}$$

(12)
using arbitrary time-dependent coefficients $a$, $b$, and $c$.

For the $\omega_+$ transition, substituting in one gets

$$\frac{\partial a}{\partial t} = i \gamma_1 B_1 \cos \beta \cos \omega t e^{-i(\epsilon_0 - \epsilon_+) t / \hbar} c(i)$$

$$\frac{\partial c}{\partial t} = i \gamma_1 B_1 \cos \beta \cos \omega t e^{-i(\epsilon_0 - \epsilon_+) t / \hbar} a(i) \quad (13)$$

If one is on resonance, with $\omega = |\epsilon_+ - \epsilon_0| / \hbar$, and dropping rapidly oscillating terms (at $2\omega$) one gets, using $\omega_1 = \gamma_1 B_1 \cos \beta$, $a_0 = a(0)$, etc.,

$$a(t) = a_0 \cos \frac{\omega_1}{2} t + i c_0 \sin \frac{\omega_1}{2} t$$

$$c(t) = c_0 \cos \frac{\omega_1}{2} t + i a_0 \sin \frac{\omega_1}{2} t$$

$$b(t) = b_0 \quad (14)$$

To compute the observed signal (for this $\omega_+$ transition) we will need $\langle I_x \rangle = \langle \psi | I_x | \psi \rangle$ during and after the RF pulse.

During the pulse

$$\langle I_x \rangle = (a_0^* a_0 - c_0^* c_0) \sin \omega_1 t \sin \omega_1^* t$$

$$+ (a_0^* c_0 e^{i \omega_1 t} + c_0^* a_0 e^{-i \omega_1 t}) \cos^2 \omega_1 t$$

$$+ (c_0^* a_0 e^{i \omega_1 t} + a_0^* c_0 e^{-i \omega_1 t}) \sin^2 \omega_1 t \quad (15)$$

For a single pulse experiment, starting from thermal equilibrium, the ensemble average of the cross-terms, $c_0^* a_0$, etc., are zero and those terms can be neglected. After a short pulse of duration $\tau$, the coefficients, $a(t)$ and $c(t)$ become time independent and one gets that

$$\langle I_x \rangle = (a_0^* a_0 - c_0^* c_0) \sin \omega_1 \tau \sin \omega_1^* \tau \quad (16)$$

It is straightforward to show that under the same conditions, $\langle I_x \rangle$ and $\langle I_y \rangle$ are time independent during the pulse.
So the signal observed in the coil with its axis along \( x' \), \( S_{x'}(t) \) is given by

\[
S_{x'}(t) \propto \cos \beta \frac{d(I_x)}{dt} = \omega_+ (a_0^* a_0 - c_0^* c_0) \cos \beta \sin \omega_1 \tau \cos \omega_3 t.
\]

Similarly one finds signals observed with orthogonal pick-up coils along \( z' \) and \( y' \) by replacing \( \cos \beta \) with \( \cos \theta \) and \( \cos \alpha \) respectively in the above equation.

For a powder sample, all possible orientations for the principal axes are present with equal probability. The signal strength will then be given by

\[
\bar{S}_{x'}(t) = 2\pi \int_0^\pi d\beta \sin \beta S_{x'}(t)
\]

\[
\propto 2\pi \omega_+ (a_0^* a_0 - c_0^* c_0) \cos \omega_3 t \int_0^\pi d\beta \sin \beta \cos \beta \sin(\gamma B_1 \tau \cos \beta)
\]

\[
= 2\pi \omega_+ (a_0^* a_0 - c_0^* c_0) \cos \omega_3 t \left[ \frac{2}{(\gamma B_1 \tau)^2} \left( \sin(\gamma B_1 \tau) - \gamma B_1 \tau \cos(\gamma B_1 \tau) \right) \right]
\]

\[
= 2\pi \omega_+ (a_0^* a_0 - c_0^* c_0) \cos \omega_3 t \left[ \frac{4\pi}{\sqrt{\gamma B_1 \tau}} J_{3/2}(\gamma B_1 \tau) \right]
\]

whereas

\[
\bar{S}_{z'}(t) = \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \cos \theta \sin(\gamma_1 B_1 \tau \sin \theta \cos \phi) = 0
\]

and similarly \( \bar{S}_{y'}(t) = 0 \).

---

1 A coil “with its axis along” a certain direction, equivalent to saying the “coil is oriented” along that direction, is taken to mean that the coil is sensitive only to the component of nuclear magnetization along that direction.
B. Circular Polarization

Now suppose instead one applies a circularly polarized RF magnetic field described by

\[ H_x = -\gamma_1 \hbar B_1 \left( I_x \cos\omega t + I_y \sin\omega t \right) \]  \hspace{1cm} (21)

For the $\omega_1$ transition, we only need the projection onto the $x$-axis. Hence,

\[ H_{\text{eff}} = -\gamma_1 \hbar B_1 \left( \sin\theta \cos\phi \cos\omega t + \sin\theta \sin\phi \sin\omega t \right) I_x \]
\[ = -\gamma_1 \hbar B_1 \sin\theta \left( \cos(\omega t - \phi) \right) I_x \]  \hspace{1cm} (22)

and so by defining $\omega_1 = \gamma_1 B_1 \sin\theta$ the analysis proceeds as before giving

\[ S_x(t) \propto \omega_1 \sin \omega_1 \tau \sin\theta \cos\phi \left( a_0^* a_0 - c_0^* c_0 \right) \cos(\omega_1 t - \phi) \]
\[ S_y(t) \propto \omega_1 \sin \omega_1 \tau \sin\theta \sin\phi \left( a_0^* a_0 - c_0^* c_0 \right) \cos(\omega_1 t - \phi) \]  \hspace{1cm} (23)

To obtain the powder average one must integrate over all angles as before. The integral over $\phi$ gives

\[ \bar{S}_x(t) = \pi \omega_1 \sin\theta \sin\omega_1 \tau \left( a_0^* a_0 - c_0^* c_0 \right) \cos\omega_1 t \]
\[ \bar{S}_y(t) = \pi \omega_1 \sin\theta \sin\omega_1 \tau \left( a_0^* a_0 - c_0^* c_0 \right) \sin\omega_1 t \]  \hspace{1cm} (24)

where the dotted bar indicates only a partial average over angles has been done. The average over $\theta$ is then

\[ \bar{S}_x(t) = \pi \omega_1 \left( a_0^* a_0 - c_0^* c_0 \right) \cos\omega_1 t \int_0^\pi d\theta \sin^2\theta \sin(\gamma B_1 \tau \sin\theta) \]
\[ = 8\pi \omega_1 \left( a_0^* a_0 - c_0^* c_0 \right) \cos\omega_1 t \left[ \frac{J_1(\gamma B_1 \tau)}{3 \cdot 1 \cdot 1} - \frac{J_3(\gamma B_1 \tau)}{5 \cdot 3 \cdot 1} - \frac{J_5(\gamma B_1 \tau)}{7 \cdot 5 \cdot 3} - \cdots \right] \]  \hspace{1cm} (25)

where the $J_n$ are Bessel functions. The signal observed along $y'$ is obtained by replacing $\cos\omega_1 t$ with $\sin\omega_1 t$ in the above equation.

This last integral above is the same as that encountered by Bloom, et al., Physical Review 97, 1699 (1955) for NQR using a spin 3/2 nucleus with $\eta = 0$ (and linear excitation and detection for a single pulse experiment). The series converges rather rapidly and the first two terms give results accurate to about 1%.
C. Effects of Inhomogeneous Line Broadening

1. Linear Polarization

Previously for the \( \omega_+ \) transition with linear polarization we had for the wavefunction coefficients (eqn (13))

\[
\frac{\partial \alpha}{\partial t} = i \gamma B_1 \cos \beta \cos \omega t e^{-i(\varepsilon - \varepsilon_+)/\hbar} c(t)
\]

\[
\frac{\partial c}{\partial t} = i \gamma B_1 \cos \beta \cos \omega t e^{-i(\varepsilon - \varepsilon_+)/\hbar} a(t)
\]

(27)

where \( \omega \) is the frequency of the applied RF excitation. Now we consider what happens if one is a bit off resonance. Writing \( \omega_+ = \omega + \Delta \omega \) and dropping the very rapidly oscillating terms, one gets the equations

\[
\frac{\partial \alpha}{\partial t} = \frac{i \omega_1}{2} e^{i \Delta \omega} c(t)
\]

\[
\frac{\partial c}{\partial t} = \frac{i \omega_1}{2} e^{-i \Delta \omega} a(t)
\]

(26)

where \( \omega_1 = \gamma_1 B_1 \cos \beta \) as before. Designating the values \( a(0) = a_0 \), etc., as before, solutions to these equations are

\[
a(t) = e^{i \Delta \omega/2} \left[ a_0 \cos(\omega_{\text{eff}} t / 2) + i \frac{\omega_1 c_0 - \Delta \omega a_0}{\omega_{\text{eff}}} \sin(\omega_{\text{eff}} t / 2) \right]
\]

\[
c(t) = e^{-i \Delta \omega/2} \left[ c_0 \cos(\omega_{\text{eff}} t / 2) + i \frac{\omega_1 a_0 + \Delta \omega c_0}{\omega_{\text{eff}}} \sin(\omega_{\text{eff}} t / 2) \right]
\]

(28)

where

\[
\omega_{\text{eff}} = \sqrt{\frac{\omega_1^2}{2} + (\Delta \omega)^2}
\]

(29)
Now compute the expectation of \( I_x \) using these coefficients

\[
\langle I_x \rangle = (a^* a |e^{i\omega t/\hbar} + c^* (0|e^{i\omega_0 t/\hbar}) I_x (a|e^{-i\omega_0 t/\hbar} + c|0)e^{-i\omega t/\hbar})
\]

\[
= a^* c e^{i\omega t} + c^* a e^{-i\omega t}
\]

(30)

If we start with thermal equilibrium, cross terms such as \( a_0^* c_0 \) will average to zero. Hence, starting from thermal equilibrium and applying the RF pulse for a time \( \tau \), one gets

\[
\langle I_x \rangle_{\text{ave}} = e^{-i\Delta \omega \tau} \left[ (a_0^* a_0 - c_0^* c_0) \left( \frac{i \omega_1}{2 \omega_{\text{eff}}} \sin(\omega_{\text{eff}} \tau) - \frac{\Delta \omega \omega_1}{\omega_{\text{eff}}^2} \sin^2(\omega_{\text{eff}} \tau / 2) \right) \right] e^{i\omega t} + c.c.
\]

(31)

or at \( t > \tau \) one has

\[
\langle I_x \rangle_{\text{ave}} = - (a_0^* a_0 - c_0^* c_0)
\]

\[
\times \left[ \frac{\omega_1}{\omega_{\text{eff}}} \sin(\omega_{\text{eff}} \tau) \sin(\omega_{\text{eff}} t - \Delta \omega \tau) + \frac{2 \Delta \omega \omega_1}{\omega_{\text{eff}}^2} \sin^2(\omega_{\text{eff}} \tau / 2) \cos(\omega_{\text{eff}} t - \Delta \omega \tau) \right]
\]

(32)

and if we assume a symmetric inhomogeneous line shape centered at \( \omega \), the terms linear in \( \Delta \omega \) will cancel and so with these assumptions this clearly reduces to the previous result when \( \Delta \omega = 0 \). For the symmetric distribution, the observed signal following an rf pulse of length \( \tau \) is then given by

\[
S_x(t) \propto (a_0^* a_0 - c_0^* c_0) \frac{\omega_1}{\omega_{\text{eff}}} \cos \beta \sin \omega_{\text{eff}} \tau \cos(\omega_{\text{eff}} (t - \tau) + \omega \tau)
\]

(33)

The powder average is given by a sum over all orientations, which has an amplitude

\[
\bar{S}_x(t) \propto 2 \pi \omega_{\text{eff}} (a_0^* a_0 - c_0^* c_0)
\]

\[
\times \int_{-\infty}^{\infty} d(\Delta \omega) \int_0^{\infty} \frac{\cos^2 \beta}{\sqrt{\cos^2 \beta + (\Delta \omega / \gamma_0 B_1)^2}} \sin^2 \left( \gamma_0 B_1 \sqrt{\cos^2 \beta + (\Delta \omega / \gamma_0 B_1)^2} \right)
\]

(34)

where \( f(\Delta \omega) \) represents the symmetric line shape. For the sake of computation, a gaussian is used,

\[
f(\Delta \omega) = \frac{1}{\sqrt{2 \pi} \sigma} e^{-(\Delta \omega^2 / 2 \sigma^2)}
\]

(35)
Results of numerical integration are shown in the attached figure.

**Figure 1** - nutation results for linearly polarized excitation for difference line widths.
2. Circular Polarization

Following the same arguments as before, one gets a factor of $\frac{1}{2}$ from the average over $\varphi$, and $\sin\beta$ replaces $\cos\beta$ in the integral. Hence, the signal expected for circular polarization and a symmetric line shape will have a magnitude given by

$$S_x(t) \propto a_1 a_2 (c_1 - c_2) \times \int_{-\infty}^{\infty} d(\Delta \omega) f(\Delta \omega) \int_{0}^{\frac{\pi}{2}} d\beta \sin\beta \frac{\sin^2 \beta}{\sqrt{\sin^2 \beta + (\Delta \omega / \gamma_1 B_1)^2}} \sin\left(\gamma_1 B_1 \tau \sqrt{\sin^2 \beta + (\Delta \omega / \gamma_1 B_1)^2}\right)$$

Results from numerical integration are shown in the attached graph.

Figure 2 - Effects of inhomogeneous line width on nutation for Circular Polarization.
Also shown are the results for a comparison of the maximum signal obtained with LP and CP excitation respectively.

\textbf{Figure 3} - Comparison of maximum signal strengths for CP and LP excitation, LP detection as the inhomogeneous line width is increased.
III. Irradiation at two frequencies, observation at the third

A. Serial Irradiation

Now consider what happens if we irradiate two of the transitions during the same experiment. The lab frame operators in terms of the molecular frame will be

\[
I_x = \cos \beta I_x + \cos \alpha \sin \beta I_y + \sin \alpha \sin \beta I_z
\]

\[
I_y = \left( \cos \alpha \cos \beta \cos \gamma - \sin \alpha \sin \gamma \right) I_x + \left( \sin \alpha \cos \beta \cos \gamma + \cos \alpha \sin \gamma \right) I_y - \sin \beta \cos \gamma I_z
\]

\[
I_y = \left( - \cos \alpha \cos \beta \sin \gamma - \sin \alpha \cos \gamma \right) I_x + \left( - \sin \alpha \cos \beta \sin \gamma + \cos \alpha \cos \gamma \right) I_y + \sin \beta \sin \gamma I_z
\]

where \( \alpha, \beta, \gamma \) are Euler angles describing the relative orientation of the molecular and lab frames. (These are not the same angles as used previously for single irradiation).

First consider “serial irradiation,” where irradiation at the two frequencies occurs at different times. First, consider an irradiation along the \( x' \) lab frame axis at the frequency \( \omega_1 \) and beginning at \( t = 0 \). The effective RF Hamiltonian is

\[
H_{\text{eff}} = - \gamma_1 \hbar B_{1-} \left( \sin \alpha \cos \beta \cos \gamma + \cos \alpha \sin \gamma \right) I_x \cos \omega t
\]

\[
= - \hbar \omega_{1-} I_x \cos \omega t
\]

Then writing the general wavefunction using time-dependent coefficients, keeping only the slowly varying terms and looking on resonance one gets

\[
\frac{\partial \alpha}{\partial t} = 0
\]

\[
\frac{\partial b}{\partial t} = \frac{\omega_{1-}}{2} c
\]

\[
\frac{\partial c}{\partial t} = - \frac{\omega_{1-}}{2} b
\]

which has solution
Now consider irradiation along the \( y' \) lab frame axis at the frequency \( \omega_0 \) starting at time \( t' \). Following the same procedure one gets an effective RF Hamiltonian

\[
H_{\text{eff}} = -\gamma _1 \hbar B_{10} \left( \sin \beta \sin \gamma \right) I_z \cos(\omega (t - t') + \varphi) \\
= -\hbar \omega_{10} I_z \cos(\omega (t - t') + \varphi)
\]  

(41)

and so

\[
\frac{\partial a}{\partial t} = i \frac{\omega_{10}}{2} e^{-i\varphi} b \\
\frac{\partial b}{\partial t} = i \frac{\omega_{10}}{2} e^{i\varphi} a \\
\frac{\partial c}{\partial t} = 0
\]  

(42)

with solutions

\[
a(t) = a(t') \cos\left(\frac{\omega_{10}}{2} (t - t')\right) + i e^{-i\varphi} b(t') \sin\left(\frac{\omega_{10}}{2} (t - t')\right) \\
b(t) = b(t') \cos\left(\frac{\omega_{10}}{2} (t - t')\right) + i e^{i\varphi} a(t') \sin\left(\frac{\omega_{10}}{2} (t - t')\right) \\
c(t) = c(t')
\]  

(43)

valid for \( t > t' \).

Combining the effects from the two pulses, with a delay of \( \tau \) between the pulses, it is straightforward to compute the wavefunction after the two pulses. If the wavefunction coefficients just before the first pulse are designated \( a_0, b_0, \) and \( c_0 \) respectively, and are assumed to have a random phase appropriate for thermal equilibrium, a signal will be produced at the sum (or
difference) frequency proportional to

\[ \langle I_x(t) \rangle = (b^*_0 b_0 - c^*_0 c_0) \sin \left( \frac{\omega_{10} \tau_y}{2} \right) \sin(\omega_1 \tau_x) \cos(\omega_+ (\tau_y + t) + \omega_- (\tau_x + \tau) - \varphi) \]  

(44)

where only terms at the frequency \( \omega_1 \) have been kept and \( t \) is the time after the second pulse. This result suggests that a signal could be observed at the third frequency, that the intensity is proportional to the population difference of the first transition excited, and that the maximum intensity is obtained if the first pulse is a “\( \pi/2 \)” pulse, and the second a “\( \pi \)” pulse. The cosine term can be written in a number of different ways by noting that \( \omega_2 = \omega_1 + \omega_0 \), and can give rise to echo-like behavior. Substituting in one obtains, for example,

\[ \langle I_x(t) \rangle = (b^*_0 b_0 - c^*_0 c_0) \sin \left( \frac{\omega_{10} \tau_y}{2} \right) \sin(\omega_1 \tau_x) \]

\[ \times \cos(\omega Q (\tau_y + \tau_x + \tau + t) + \frac{\omega Q \eta}{3} (t + \tau_y - \tau - \tau_x) - \varphi) \]

(45)

hence a distribution in the values of \( \eta \) will be refocused when \( t = \tau + \tau_x - \tau_y \). A distribution of \( \omega_0 \) is not refocused by this sequence, implying that one should keep \( \tau \) as short as possible. A simple examination of the equations above suggests that the equivalent of a “\( \pi \)” pulse between the \(|+\rangle\) and \(|0\rangle\) states might be obtained by applying a sequence \( \pi_x - \pi_y - \pi_x \), where \( \pi_x \) corresponds to a \( \pi \) pulse applied along the \( x \) direction (at frequency \( \omega_1 \)) and \( \pi_y \) to a \( \pi \) pulse along \( y \) (at frequency \( \omega_0 \)). Hence, using this serial excitation one might expect to form a Hahn-type echo at \( \omega_1 \) using a sequence of five pulses with appropriate delays.

The question remains whether or not one obtains an observable signal for a powder sample. The signal measured along the \( z \) direction will be proportional to the powder average of

\[ \langle S \rangle_z \propto \cos \alpha \sin \beta \frac{d(I_x)}{dt} \]  

(46)

Writing in the angular dependence for \( \omega_1 \) and \( \omega_{10} \) and keeping only terms which are even in both the angles \( \alpha \) and \( \gamma \), one ultimately must evaluate

\[ \int_0^{2\pi} d\gamma \int_0^{2\pi} d\alpha \int_0^{\pi} d\beta \sin \beta \]

\[ \times \cos \alpha \sin \beta \sin(A \sin \beta \sin \gamma) \sin(B \cos \alpha \sin \gamma) \cos(B \sin \alpha \cos \beta \cos \gamma) \]

(47)
where

\[ A = \frac{\gamma_1 B_0 \tau_y}{2} \]
\[ B = \gamma_1 B_1 \tau_x \]  

(48)

To see what this looks like, this integration was performed numerically for the case \( A = B \).

**Figure 4** - relative signal amplitude at \( \omega_z \) observed along the \( z \)-direction for sequential excitation as described.
Now look at the effects of inhomogeneity for the serial 3f serial excitation.

For the excitation at $\omega_0$, the equations to solve are

$$\frac{\partial a}{\partial t} = \frac{i \omega_{10}}{2} e^{i \Delta \omega_0 t} \, b$$
$$\frac{\partial b}{\partial t} = \frac{i \omega_{10}}{2} e^{-i \Delta \omega_0 t} \, a$$

where $\omega_0 = \omega + \Delta \omega_0$. This is essentially the same equation as seen above for $\omega$, and so will have solution

$$a(t) = e^{i \Delta \omega_0 t/2} \left[ a_0 \cos(\omega_{e0} t / 2) + i \frac{\omega_{10} b_0 - \Delta \omega_0 a_0}{\omega_{e0}} \sin(\omega_{e0} t / 2) \right]$$
$$b(t) = e^{-i \Delta \omega_0 t/2} \left[ b_0 \cos(\omega_{e0} t / 2) + i \frac{\omega_{10} a_0 + \Delta \omega_0 b_0}{\omega_{e0}} \sin(\omega_{e0} t / 2) \right]$$

where $c(t)$ is constant, and

$$\omega_{e0} = \sqrt{\omega_{10}^2 + (\Delta \omega_0)^2}$$

and for excitation at $\omega_0 = \omega - \Delta \omega_0$, one gets

$$\frac{\partial b}{\partial t} = \frac{\omega_{1-}}{2} e^{i \Delta \omega_{-} t} \, c$$
$$\frac{\partial c}{\partial t} = -\frac{\omega_{1-}}{2} e^{-i \Delta \omega_{-} t} \, b$$

which has solutions

$$b(t) = e^{i \Delta \omega_{-} t/2} \left[ b_0 \cos(\omega_{e-} t / 2) + \frac{\omega_{1-} c_0 - i \Delta \omega_{-} b_0}{\omega_{e-}} \sin(\omega_{e-} t / 2) \right]$$
$$c(t) = e^{-i \Delta \omega_{-} t/2} \left[ c_0 \cos(\omega_{e-} t / 2) - \frac{\omega_{1-} b_0 - i \Delta \omega_{-} c_0}{\omega_{e-}} \sin(\omega_{e-} t / 2) \right]$$
where \( a(t) \) is constant, and

\[
\omega_{\varepsilon^-} = \sqrt{\omega_{\varepsilon^-}^2 + (\Delta \omega_{\varepsilon^-})^2}
\]  

(54)

So now, we start at thermal equilibrium, apply a pulse at \( \omega_{\varepsilon^-} \) for a time \( t \), then delay a time \( \tau \), followed by a pulse at \( \omega_{\varepsilon^0} \) for a time \( t_0 \).

Assuming a symmetric distribution for the transitions and that the applied RF is adjusted to the center frequency of the appropriate distribution, the resultant magnitude of the signal at \( \omega_{\varepsilon^-} \) immediately after the 2\(^{nd}\) pulse will look something like the powder average of

\[
S_x \propto \cos \beta \frac{\omega_{\varepsilon^-}}{\omega_{\varepsilon^0}} \left[ b_0^* b_0 - c_0^* c_0 \right] \sin(\omega_{\varepsilon^-} t) \sin(\omega_{\varepsilon^0} t_0 / 2)
\]

\[
\times \cos(\Delta \omega_{\varepsilon^-} t_0 / 2 + \Delta \omega_{\varepsilon^-} (t_0 + \tau))
\]  

(55)

In general, the frequency distributions for the various transitions are not independent. For example, if the distribution is due to a distribution in \( \nu_0 \), then

\[
\Delta \omega_{\varepsilon^-} = \frac{\omega_{\varepsilon^-}}{\omega_{\varepsilon^0}} \Delta \omega_{\varepsilon^0}
\]  

(56)

Note that the last cosine term will result in a significant change in the response for longer pulse lengths compared to shorter pulse lengths.

**B. Simultaneous irradiation**

For the case of simultaneous irradiation of the \( \omega_{\varepsilon^-} \) and \( \omega_{\varepsilon^0} \) transitions, the following need to be solved:

\[
\frac{\partial a}{\partial t} = i \frac{\omega_{\varepsilon^0}}{2} e^{-i\theta} b
\]

\[
\frac{\partial b}{\partial t} = i \frac{\omega_{\varepsilon^0}}{2} e^{i\theta} a + \frac{\omega_{\varepsilon^-}}{2} c
\]

\[
\frac{\partial c}{\partial t} = -\frac{\omega_{\varepsilon^-}}{2} b
\]  

(57)
As a first observation, take the derivative of the first and last, and then substitute in the second to get

\[
\frac{\partial^2 a}{\partial t^2} = -\frac{\omega_{10}^2}{4} a + i \frac{\omega_{10}\omega_{1-}}{4} e^{-i\varphi} c
\]
\[
\frac{\partial^2 c}{\partial t^2} = -\frac{\omega_{1-}^2}{4} c - i \frac{\omega_{10}\omega_{1-}}{4} e^{i\varphi} a
\]

This is a simple eigenvalue problem (i.e. Assume a periodic solution, which results in a set of homogeneous equations. Set the determinant equal to zero to find the allowed solutions, then take linear combinations of those solutions to match the initial conditions.). This shows that the time dependence of \(a\) and \(c\) can be determined, in principle, independently of \(b\), and so one might anticipate an effective spin-\(\frac{1}{2}\)-like solution, to some extent.

Assuming a periodic solution and using the three first-order equations above, it is easy to find three eigenfrequencies, one of which is zero and the other two are

\[
\pm \frac{\omega_{\text{eff}}}{2} = \pm \frac{1}{2} \sqrt{\omega_{10}^2 + \omega_{1-}^2}
\]

and the corresponding eigenvectors (in \(a, b, c\) order vertically) are

\[
\frac{1}{\omega_{\text{eff}}} \begin{pmatrix} \omega_{1-} \\ 0 \\ -i \omega_{10} e^{i\varphi} \end{pmatrix}, \quad \frac{1}{\sqrt{2}} \frac{1}{\omega_{\text{eff}}} \begin{pmatrix} \omega_{10} e^{-i\varphi} \\ \pm \omega_{\text{eff}} \\ i \omega_{1-} \end{pmatrix}
\]

appropriate linear combinations of these are formed to yield
The signal at the frequency $\omega_i$ is proportional to

$$\langle I_x(i) \rangle = \left[ a^*(t)c(t)e^{i\omega_it} + c^*(t)a(t)e^{-i\omega_it} \right]$$

(62)

If we start with coefficients of the wavefunction appropriate for thermal equilibrium, then after an RF pulse of duration $t_p$

$$\langle I_x(t) \rangle = 2\left( \frac{\omega_{10} \omega_{1-}}{\omega_{\text{eff}}} \right) \sin(\omega_{\text{eff}}t_p/2) \sin(\omega_{\text{eff}}t + \varphi) \times \left[ \left( \frac{\omega_{10}^2}{\omega_{\text{eff}}} + \frac{\omega_{1-}^2}{\omega_{\text{eff}}} \cos(\omega_{\text{eff}}t_p/2) \right) a_0^*a_0 + \left( \frac{\omega_{10}^2}{\omega_{\text{eff}}} + \frac{\omega_{1-}^2}{\omega_{\text{eff}}} \cos(\omega_{\text{eff}}t_p/2) \right) c_0^*c_0 - \left( 1 + \cos(\omega_{\text{eff}}t_p/2) \right) b_0^*b_0 \right]$$

(63)
It will be convenient to define \( \cos \zeta = \omega_{10}/\omega_{\text{eff}}, \sin \zeta = \omega_j/\omega_{\text{eff}}, \) and \( \theta = \omega_{\text{eff}} t/2 \) giving

\[
\langle I_x(t) \rangle = 2 \sin \zeta \cos \zeta (1 - \cos \theta) \sin (\theta + t + \varphi) \\
\times \left[ \sin^2 \zeta + \cos^2 \zeta \cos(\theta) \right] a_0^* a_0 + \left( \cos^2 \zeta + \sin^2 \zeta \cos(\theta) \right) c_0^* c_0 - (1 + \cos(\theta)) b_0^* b_0 \tag{64}\]

To get a feel for what this means, consider the case where \( \omega_{1-} = \omega_{10} = \omega_{\text{eff}}/\sqrt{2} \), then

\[
\langle I_x(t) \rangle = \left[ (a_0^* a_0 - b_0^* b_0) - (b_0^* b_0 - c_0^* c_0) \right] \sin^2 \left( \frac{\omega_{\text{eff}} t}{2} \right) \sin (\theta + t + \varphi) \tag{65}\]

which depends on the difference of the population differences for the two excited transitions.

In the high temperature approximation, the thermal populations of the levels are given by

\[
3a_0^* a_0 = 1 - \frac{\epsilon_-}{k_B T}, \quad 3b_0^* b_0 = 1 - \frac{\epsilon_-}{k_B T}, \quad 3c_0^* c_0 = 1 - \frac{\epsilon_0}{k_B T} \tag{66}\]

and so for this case

\[
\langle I_x(t) \rangle = (1 - \eta) \frac{\hbar \omega \varphi}{3 k_B T} \sin^2 \left( \frac{\omega_{\text{eff}} t}{2} \right) \sin (\theta + t + \varphi) \tag{67}\]

and hence a signal should be observed.

Now look at the case where \( \omega_{\text{eff}} t/2 = \pi \) (still with \( \omega_{1-} = \omega_{10} = \omega_{\text{eff}}/\sqrt{2} \)). If one starts from thermal equilibrium, no signal is expected. However looking at the change in the wavefunction coefficients, one gets

\[
a(t) = i e^{-i\varphi} c(0) \\
b(t) = -b(0) \\
c(t) = -i e^{i\varphi} a(0) \tag{68}\]
which looks like the results of a “π” pulse between the |+⟩ and |0⟩ states. Hence, once coherence is created between the |+⟩ and |0⟩ states, one can expect to be able to form echoes using such a pulse.

The results for a single pulse are less obvious for the powder average. It is straightforward to show that, for the powder average, no signal is observed using receiving coils oriented in the x-y plane in any case. It is also straightforward to show that for the case where $B_{1-} = B_{10}$ that the signal is proportional to $(1-\eta)$. The general case is less obvious. The signal amplitude observed by a coil oriented for detection along the z-direction was calculated numerically for several different cases. Plots of the results can be found on the following pages. It is interesting to note that as a result of the powder average, the largest signals can be found when $B_{10} \approx 2B_{1-}$, a condition similar to that found for serial pulses.

It is noted that in the limit of small excitation, such as would be used for CW experiments, the observed signal will be proportional to

$$\langle I_x \rangle \approx 2\, \omega_{10} \, \omega_{1-} \, (3 - \eta) \, \tau^2 \tag{69}$$

where $\tau$ is related to $T_1$ and $T_2$. This signal could be quite weak. It is also noted that for the same reason these 2f processes can be neglected when computing $T_1$ due to the small time dependent terms arising from thermal fluctuations.

The 2f process illustrated here is for excitations at $\omega_0$ and $\omega_-$. If instead, one were to excite at $\omega_-$ and $\omega_+$, the equations to solve will be

$$\frac{\partial a}{\partial t} = i \frac{\omega_+}{2} \, c \tag{70}$$
$$\frac{\partial c}{\partial t} = i \frac{\omega_+}{2} \, a - \frac{\omega_-}{2} \, b$$
$$\frac{\partial b}{\partial t} = \frac{\omega_-}{2} \, c$$

which, aside from name changes, is essentially identical to eqn (56), and hence a similar result should be expected.
Figure 5 - Relative signal amplitude observed along the z-direction for $\omega$, following a single rf pulse applied simultaneously at $\omega_0$ and $\omega_0$. 

$$B_{10} = B_{1-}$$

$\eta = 0.1$

$0.3$

$0.5$

$0.7$

$0.9$

Signal Amplitude (arb)

$\gamma B_{1-} \tau$
Figure 6 - Similar to previous figure, but for unequal excitation fields.
IV. Operator Methods

A. General Results

Examination of equations (14), (39), (42), and (60), and using identities for \( I = 1 \), one finds that for an RF pulse of duration \( t_p \) along the z-direction at a frequency \( \omega_0 \), the change in the wavefunction coefficients \( a, b, \) and \( c \) can be found using a simple rotation of the original wavefunction, that is

\[
|\psi(\tau)\rangle = e^{-i\hat{H}\tau/\hbar} e^{i\hat{I} \cdot \hat{\theta}} |\psi(0)\rangle
\]  

(71)

where \( \hat{\theta} = \omega_0 t_p / 2 \). Similarly an RF pulse along the y-direction at the frequency \( \omega_i \) is equivalent to a rotation about \( y \), etc.

The double irradiation case is more tedious. For the case where \( \varphi = 0 \) it is easily shown to be equivalent to a rotation about an axis in the y-z plane, rotated from the z-axis by an angle \( \xi \), where \( \cos \xi = \omega_{10}/\omega_{\text{eff}} \). That is

\[
|\psi(\tau)\rangle = e^{-i\hat{H}\tau/\hbar} e^{i(\cos \xi I_z + \sin \xi I_y) \hat{\theta}} |\psi(0)\rangle
\]  

(72)

where \( \hat{\theta} = \omega_{\text{eff}} t_p / 2 \). This rotation is somewhat inconvenient to use in practice, but can be replaced by a sequence of rotations about the x and z axis. That is,

\[
e^{i(\cos \xi I_z + \sin \xi I_y) \hat{\theta}} = e^{iI_z^\xi} e^{iI_y^\theta} e^{-iI_x^\xi}
\]  

(73)

The case where \( \varphi \neq 0 \) will be addressed later.

When in thermal equilibrium and in the high temperature limit, the density matrix operator is given by

\[
\rho(0) = \frac{1}{3} \left( 1 - \frac{\hat{H}_\varphi}{k_B T} \right)
\]

\[
= \frac{1}{3} \left( 1 - \frac{\hbar \omega}{3 k_B T} \left[ (1 + \eta)(1 - I_z^2) + (1 - \eta)(1 - I_x^2) - 2(1 - I_y^2) \right] \right)
\]  

(74)

\[
= \frac{1}{3} \left( 1 - \frac{\hbar \omega}{3 k_B T} \left[ 3I_z^2 + \eta(I_x^2 - I_y^2) - I_z^2 \right] \right)
\]
and the signals of interest will involve the computation of \( \text{Tr}(I_{\alpha} \rho) \), \( \alpha = x, y, \) or \( z \). The terms which are constant under rotation will not contribute to the signal, and hence one can use a reduced density matrix, 

\[
\rho(0) = 3I_z^2 + \eta (I_x^2 - I_y^2)
\]  

(75)

to perform calculations.

B. Single-Pulse Sequences

The signal, \( s(t) \), for a single frequency, single pulse NQR experiment using the \( \omega_0 \) transition would be found by computing

\[
\rho'(\tau) = e^{i\omega_0 \tau} \rho(0) e^{-i\omega_0 \tau}
\]

\[
= 3I_z^2 + \eta \left[ \cos 2\theta (I_x^2 - I_y^2) + \sin 2\theta (I_xI_y + I_yI_x) \right]
\]

\[
\rho(t) = e^{-iH_0 t/\hbar} \rho'(\tau) e^{+iH_0 t/\hbar}
\]

\[
m_z(t) \propto \text{Tr}(I_z \rho(t)) = \langle + | \rho(t) | - \rangle + \langle - | \rho(t) | + \rangle
\]

\[
= \langle + | \rho'(\tau) | - \rangle e^{-i\omega_0 \tau} + \langle - | \rho'(\tau) | + \rangle e^{+i\omega_0 \tau}
\]

\[
= 2\eta \sin 2\theta \sin \omega_0 t
\]

\[
s(t) \propto \frac{dm_z}{dt} \propto 2\omega_0 \eta \sin 2\theta \cos \omega_0 t = 2\omega_0 \eta \sin \omega_0 \tau \cos \omega_0 t
\]  

(76)

Now the above calculation can be made to look simpler if new operators, \( I_z^+ \) and \( I_z^- \), are created, for which all the matrix elements are zero except

\[
\langle + | I_z^- | - \rangle = 1 \quad \langle - | I_z^- | + \rangle = 1
\]

\[
I_z^+ = -iI_xI_y \quad I_z^- = iI_yI_x
\]

\[
I_z = I_z^+ + I_z^-
\]  

(77)

and so one can write

\[
m_{z+}(t) \propto \text{Tr}(I_z^+ \rho(t)) = \langle - | \rho(t) | + \rangle
\]

\[
m_z(t) = 2 \Re(m_{z+}(t))
\]

(78)

Note that these new operators are non-Hermitian, and hence do not correspond to separate
observables. In some sense, \( m_z^+ \) and \( m_z^- \) can be thought of as “counter-rotating magnetizations,” though, in fact, individually they are not real magnetizations. Alternatively one might use \( I_z \) and \( I_z^* = i(\dot{I}_z + I_z) \) where \( I_z^* \) is not observable, instead of using \( I_z^+ \) and \( I_z^- \).

Now, returning to the double irradiation case, now with \( \varphi \neq 0 \), the effect of a pulse is a unitary transformation, which looks a lot like a rotation but with an extra phase shift

\[
|\psi(t)\rangle = e^{-iH_{rf}t/\hbar} \left[ (1 - K^2) + K^2 \cos \vartheta + iK \sin \vartheta \right] |\psi(0)\rangle
\]

\[
K = \sin \xi I_y + \cos \xi \left( \cos \varphi I_z - \sin \varphi (I_x I_y + I_y I_x) \right)
\]

\[
= \sin \xi I_y + \cos \xi \left( I_{z+} e^{-i\varphi} + I_{z-} e^{i\varphi} \right)
\]

As was seen in eqn. (43) and (44), the net effect of this phase shift is an overall shift in phase of the observed signal.

The results shown in eqn. (60) can be easily generalized for the case where the pulse at frequency \( \omega_0 \) is applied with phase \( \varphi_y \), and the pulse at frequency \( \omega_0 \) is applied with phase \( \varphi_z \), and defining

\[
I_{y+} = -iI_z I_x \quad I_{y-} = iI_x I_z
\]

(80)

giving

\[
K = \sin \xi \left( I_{y+} e^{-i\varphi_y} + I_{y-} e^{i\varphi_y} \right) + \cos \xi \left( I_{z+} e^{-i\varphi_z} + I_{z-} e^{i\varphi_z} \right)
\]

(81)

If our two RF sources are applied exactly on resonance, and if at some time, \( t' = 0 \), both RF sources have a phase of 0, then after a time \( t' \), \( \varphi_y = \omega_0 t' \) and \( \varphi_z = \omega_0 t' \), so eqn. (80) is equivalent to

\[
K = e^{-iH_{rf}t'/\hbar} K_0 e^{iH_{rf}t'/\hbar}
\]

(82)

where

\[
K_0 = \cos \xi I_z + \sin \xi I_y
\]

(83)

Equation (81) can be interpreted as “go back in time to where the phases were zero, do the change, then go back forward in time again.”

Using this result, equation (78) becomes

\[
|\psi(t)\rangle = e^{-iH_{rf}t/\hbar} \left( e^{-iH_{rf}t'/\hbar} e^{iK_0} e^{iH_{rf}t'/\hbar} \right) |\psi(0)\rangle
\]

(84)
A similar equation is obtained if the RF phases of the two pulses are not zero (or if there is no time when they are both zero). To see this, write the effects of the 2-frequency RF pulse with arbitrary phases as

$$|\psi(t)\rangle = U^{-1} e^{iH_0 t} U |\psi(0)\rangle$$

(85)

where the effects of the transformation due to the operator $U$ are expressed conveniently in terms of what happens to the products of the spin operators. In particular,

$$
\begin{align*}
I_x I_y &\Rightarrow e^{-i\theta_x} I_x I_y \\
I_y I_x &\Rightarrow e^{i\theta_y} I_y I_x \\
I_z I_x &\Rightarrow e^{-i\theta_z} I_z I_x \\
I_x I_z &\Rightarrow e^{i\theta_z} I_x I_z \\
I_z I_y &\Rightarrow e^{-(\theta_z + \theta_y)} I_z I_y \\
I_y I_z &\Rightarrow e^{(\theta_z + \theta_y)} I_y I_z \\
I_z I_z &\Rightarrow I_z I_z \\
I_x I_x &\Rightarrow I_x I_x \\
I_y I_y &\Rightarrow I_y I_y
\end{align*}
$$

(86)

Note that, using the usual commutation relation for angular momentum, each spin operator can always be written in terms of the products of two operators. If one compares this to the time evolution due to the quadrupole Hamiltonian

$$
\begin{align*}
e^{-iH_d t/\hbar} I_x I_y e^{iH_d t/\hbar} &= e^{-i\omega_{xy} t} I_x I_y \\
e^{-iH_d t/\hbar} I_z I_x e^{iH_d t/\hbar} &= e^{-i\omega_{zx} t} I_z I_x \\
e^{-iH_d t/\hbar} I_z I_y e^{iH_d t/\hbar} &= e^{-i\omega_{zy} t} I_z I_y \\
e^{-iH_d t/\hbar} I_z I_z e^{iH_d t/\hbar} &= I_z I_z \\
e^{-iH_d t/\hbar} I_y I_x e^{iH_d t/\hbar} &= I_y I_x \\
e^{-iH_d t/\hbar} I_x I_x e^{iH_d t/\hbar} &= I_x I_x
\end{align*}
$$

(87)

It is clear that the operator $U$ can be expressed as

$$U^{-1} = e^{-iH_0' t'/\hbar}$$

(88)

for an appropriately chosen fictitious quadrupole Hamiltonian, $H_0'$, and time, $t'$. That is

$$
\begin{align*}
H_0' t' &= \frac{\hbar \omega_{d} t'}{3} \left((3I_z^2 - I_x^2) + \eta'(I_x^2 - I_y^2)\right) \\
\omega_{d} t' &= (2\omega_y + \omega_z) / 2 \\
\eta' &= \frac{3\omega_z}{2\omega_y + \omega_z}
\end{align*}
$$

(89)
Note that the usual restriction that $0 \leq \eta' \leq 1$ is not being enforced here, since the principal axes are determined by the real quadrupole Hamiltonian, and also note that the time, $t'$, which appears in these equations can be chosen for convenience. If the only phase shift is due to the time evolution, then the previous result is obtained. It is important to note that $H_{Q'}$ has the same principal axes as does $H_{Q}$, and hence $H_{Q'}$ will commute with $H_{Q}$. Thus, the phase shift due to time evolution alone can be treated as before, and the use of $H_{Q'}$ will be reserved for additional phase shifts imposed by the experimenter. (In NMR, the phase shifts due to the time evolution are addressed using the “rotating frame,” and additional phase shifts correspond to a change in direction of the applied RF within the rotating frame. The same philosophy is being used here).

It is now straightforward to compute the results of a single $2\pi$ pulse:

\[
\rho(t) = e^{-iH_{Q}t} e^{-iH_{Q} \eta' t} e^{iH_{Q} \eta' t} e^{iH_{Q} \eta' t} \\
= e^{-iH_{Q}t} e^{-iH_{Q} \eta' t} e^{iH_{Q} \eta' t} (3I_{x}^{2} + \eta(I_{x}^{2} - I_{y}^{2})) e^{-iH_{Q} \eta' t} e^{iH_{Q} \eta' t} \\
= e^{-iH_{Q}t} e^{-iH_{Q} \eta' t} \{ \eta \}
\]

\[
\begin{align*}
I_{x}^{2} & \left[ 3(\cos^{2} \xi + \sin^{2} \xi \cos \theta)^{2} + \eta \sin^{2} \xi (\sin^{2} \theta - \cos^{2} \xi (1 - \cos \theta)^{2}) \right] \\
+ I_{y}^{2} & \left[ 3(\cos^{2} \xi \sin^{2} \xi (1 - \cos \theta)^{2} + \eta (\sin^{2} \theta \cos^{2} \xi - (\sin^{2} \xi + \cos^{2} \xi \cos \theta)^{2}) \right] \\
+ I_{z}^{2} & \left[ 3 \sin^{2} \xi \sin^{2} \theta + \eta (\cos^{2} \theta - \cos^{2} \xi \sin^{2} \theta) \right] \\
+ (I_{x} I_{y} + I_{y} I_{x}) & \sin \xi \cos \xi (\cos \theta - 1) \left[ 3(\cos^{2} \xi + \sin^{2} \xi \cos \theta) - \eta (1 + \cos \theta + \sin^{2} \xi + \cos^{2} \xi \cos \theta) \right] \\
+ (I_{x} I_{y} + I_{y} I_{x}) & \sin \theta \sin \xi \left[ -3(\cos^{2} \xi + \sin^{2} \xi \cos \theta) + \eta (\cos \theta - \cos^{2} \xi (1 - \cos \theta)) \right] \\
+ (I_{x} I_{y} + I_{y} I_{x}) & \sin \theta \cos \xi \left[ 3 \sin^{2} \xi (1 - \cos \theta) + \eta (\cos \theta + (\sin^{2} \xi + \cos^{2} \xi \cos \theta)) \right]
\}
\]

and the last step can be accomplished using the relationships shown in eqns. (85) and (86). The first three terms in brackets of eqn. (89) do not give rise to a time-dependent magnetization. The last three give rise to time-dependent magnetizations along the x, y, and z-directions with frequencies $\omega_{x}$, $\omega_{y}$, and $\omega_{z}$ respectively.

As an example, the magnetization at $\omega_{y}$ depends only on the term involving $(I_{x} I_{y} + I_{y} I_{x})$. An examination of the trigonometric terms shows that that magnetization will be a maximum when $\theta = \pi$ and $\xi = \pi/8$ (or $3\pi/8$). Using those values, one gets
which is the same as what one would get by applying a \( \pi/2 \) pulse at \( \omega \). Note that using serial irradiation the amplitude of the signal depended on the initial population difference for the first transition excited. With the 2f pulse, the population difference between the two observed levels is what is obtained (for the maximum signal). This has implications for signal enhancing techniques (for example, exciting at \( \omega_n \) and \( \omega_0 \), in order to more efficiently observe at \( \omega_0 \)).

One interesting feature is to note that a single pulse twice as long corresponds to a rotation of \( 2\pi \) which leaves the thermal equilibrium density matrix unchanged. Hence, an initial \( \pi \) pulse, such as what one might wish to use for an inversion-recovery measurement of \( T_1 \), is not possible.

### C. Two-Pulse Sequences - Spin Echoes

Now in practice, we expect a small distribution of quadrupole interactions within the sample, and hence it is impossible to apply RF pulse “exactly on resonance” for all nuclei simultaneously. If we write

\[
H_Q = H_Q^{(0)} + \Delta H_Q
\]

\[
= H_Q^{(0)} + H_Q^{(1)} + H_Q^{(2)} + \ldots
\]

(92)

where \( H_Q^{(1)} \) is the secular part (i.e., it commutes with \( H_Q^{(0)} \)) of the perturbation, \( \Delta H_Q \), and assume the higher order terms are negligible, eqn. (83) becomes

\[
|\psi(t)\rangle = e^{-iH_0^{(0)}t/\hbar} e^{-iH_0^{(1)}t/\hbar} \left( e^{-iH_0^{(0)}t'/\hbar} e^{i\varphi} e^{+iH_0^{(0)}t'/\hbar} \right) |\psi(0)\rangle
\]

(93)

It is assumed that \( H_Q^{(1)} \) is small enough that it has a negligible effect on the time evolution during applied pulses so that for single frequency experiments, the effect of the pulse is still a simple rotation, and for the 2f excitation, no alteration in \( K_0 \) is necessary (this is the usual “large-pulse approximation”). We will also assume that the RF phase(s) is (are) zero for the first pulse.

In terms of the density matrix operator, what is needed to describe a two pulse sequence, with a time, \( \tau \), between the pulses is
\[\rho(t) = e^{-iH_0^0 t} e^{-iH_1^0 t} \left( e^{-iH_0^0 t} e^{i\theta_1} e^{i\theta_2} e^{-iH_0^0 t} e^{i\theta_1} \right) \left( e^{-iH_0^0 t} e^{i\theta_1} e^{i\theta_2} e^{-iH_0^0 t} e^{i\theta_1} \right) \rho(0) (h.c.) \]

\[= e^{-iH_0^0 (t+\tau) / \hbar} e^{-iH_1^0 (t+\tau) / \hbar} e^{i\theta_1} e^{i\theta_2} e^{-iH_0^0 (t+\tau) / \hbar} e^{i\theta_1} \rho(0) (h.c.) \]

where \(t\) is the time after the beginning of the second pulse, \(\theta_1\) and \(\theta_2\) are the “tilt angles”\(^1\) for the two pulses respectively, and “h.c.” is the Hermitian conjugate of the operators on the left side of the equation. For single frequency excitation, \(K_0\) is replaced by the appropriate angular momentum operator.

1. Single Frequency Echoes

Consider a single frequency experiment done for the \(\omega_1\) transition. Then

\[
\rho(t) = e^{-iH_0^0 (t+\tau) / \hbar} e^{-iH_1^0 (t+\tau) / \hbar} \left( e^{-iH_0^0 (t+\tau) / \hbar} e^{i\theta_1} e^{i\theta_2} e^{-iH_0^0 (t+\tau) / \hbar} e^{i\theta_1} \right) \left( 3I_z^2 + \eta (I_x^2 - I_y^2) \right) (h.c.)
\]

\[= e^{-iH_0^0 (t+\tau) / \hbar} e^{-iH_1^0 (t+\tau) / \hbar} e^{i\theta_1} e^{i\theta_2} \times \]

\[
\left\{ I_z^2 \left( 3 \cos^2 \theta_1 - \eta \sin^2 \theta_1 \right) + I_x^2 \eta + I_y^2 \left( 3 \sin^2 \theta_1 - \eta \cos^2 \theta_1 \right) + (I_x I_y e^{i(\omega_1^0 t - \varphi_1)} + I_x I_y e^{-i(\omega_1^0 t + \varphi_1)})(3 + \eta) \sin \vartheta_1 \cos \vartheta_1 \right\} (h.c.)
\]

\[= \left( \frac{3 + \eta}{2} \right) \sin 2\vartheta_1 \sin^2 \vartheta_2 \left( I_y I_x e^{i(\omega_1^0 (t+\tau) + 2\varphi_1)} e^{i\omega_1 (t+\tau)} + I_x I_y e^{-i(\omega_1^0 (t+\tau) + 2\varphi_1)} e^{-i\omega_1 (t+\tau)} \right)
\]

\[+ \ldots
\]

where in the last step, only those terms which refocus are written out explicitly. The echo at \(t = \tau\) will be a maximum when \(\theta_1 = \pi/4\) (which is the “90° pulse” for this experiment) and \(\theta_2\) is twice \(\theta_1\) – that is, the usual “Hahn echo.” Since no relaxation effects have been included, the amplitude of the echo is equal to the magnitude of the FID after a single 90° pulse.

\(^1\) The term “90° pulse” is reserved for the pulse length which yields the largest FID signal. In general, that does not correspond to \(\theta = 90°\), hence “tilt angle” is put in quotes.
2. 2-frequency echoes

The general result for a two-pulse 2f excitation is quite complicated. To start with, consider the first pulse to have $\xi_1 = \pi/8$ and $\vartheta_1 = \pi$, as in equation (90). It will be assumed that the phases of the two RF pulses are both zero for the first pulse. Only terms from eqn. (89) which refocus will be kept. Hence, the terms involving $I_x^2$, $I_y^2$, and $I_z^2$ will not contribute to the echo. Furthermore, only the echo at $\omega_1$ will be computed, and so only terms involving $I_yI_z$ and $I_zI_y$ need to be kept after the second pulse. Only some of those terms refocus and the remaining are not written here.

Denoting the relevant portion of the density matrix as $\rho_x$, one then needs to compute

$$\rho_x(t) = e^{-iH_0(t+\tau)/\hbar} e^{-iH_1't/\hbar} e^{i\xi_1\vartheta_1} e^{iH_d't} e^{i\xi_2\vartheta_2} e^{iH_d't} \left[ -\frac{3+\eta}{2} (I_yI_x e^{i\omega_1't} + I_zI_y e^{i\omega_1't}) \right] (\text{h.c.})$$

$$= \left( -\frac{3+\eta}{2} \right) e^{-iH_0(t+\tau)/\hbar} \left[ \sin^2 \xi_2 \cos^2 \xi_2 (1-\cos \vartheta_2)^2 \left( I_yI_x e^{i\omega_1'(t+\tau)-2\varphi} + I_zI_y e^{-i\omega_1'(t+\tau)-2\varphi} \right) \right]$$

where $\varphi = \varphi_1 + \varphi_2$. One can see that complete refocusing (of the secular part of $\Delta H_0$) occurs when $\xi_2 = \pi/4$ and $\vartheta_2 = \pi$. That is, to most efficiently form the echo, the relative amplitudes of $B_{1x}$ and $B_{1y}$ change between the first and second pulse, but $\omega_{\text{eff}} t_p$ for the second pulse is the same as for the first pulse.

This echo can be regarded as a cousin to the “Solid Echo” sequence (also known as the “Quadrupole Echo”) used in NMR which is known to refocus a perturbing quadrupole interaction in high magnetic fields (J H Davis, et al., Chem. Phys. Lett. 42, 390 (1976)). For the NMR solid echo, the two applied pulses have the same nutation angle ($\pi/2$) but are applied $90^\circ$ out of phase. The phase shift corresponds to a rotation of the effective RF field in the rotating frame. Equally well, although inconvenient in practice, the NMR solid echo could be implemented using two in-phase, orthogonal RF fields in the lab frame where the effective RF field is rotated $90^\circ$ between the two pulses. Here, for this “2f NQR echo,” the two pulses also have the same nutation angle and the effective RF field (which is the combination of $B_{1x}$ and $B_{1y}$ along perpendicular axes) is rotated in the lab frame.

The second pulse has a simple interpretation. If one starts with

$$I_x = i(I_yI_z - I_zI_y)$$

then a rotation of $180^\circ$ about an axis in the y-z plane, $45^\circ$ from the z-axis rotates y into z, z into y and x into -x, and hence the result is
and so any magnetization along the x-direction is inverted by such a pulse.

Following a similar analysis starting from eqn. (89) and keeping only those terms completely refocused and which result in an RF magnetization at frequency \( \omega_1 \), one obtains

\[
\rho(t) = (I_x I_y e^{i(\omega_1 t - \tau - 2\varphi)} + I_x I_y e^{-i(\omega_1 t - \tau + 2\varphi)}) 
\times 
\frac{1}{8} \sin 2\xi_1 (\cos \theta_1 - 1) \left[ 3(\cos^2 \xi_1 + \sin^2 \xi_1 \cos \theta_1) - \eta ((1 + \sin^2 \xi_1) + (1 + \cos^2 \xi_1) \cos \theta_1) \right] 
\times 
\sin^2 2\xi_1 (1 - \cos \theta_2)^2 
+ \ldots
\]

which can be used to compute the powder average. Unfortunately, there are many variables present (remember also that \( \xi_1, \xi_2, \theta_1, \) and \( \theta_2 \) are all orientation dependent). The results of numerical powder averages for a few specific cases are shown on the following page. For these calculations the horizontal axis corresponds to \( \gamma_i B_{10} t_p \) for the first pulse. Each curve is labeled with three numbers which are the corresponding relative sizes of \( \gamma_i B_{10} t_p \) for the first pulse, \( \gamma_i B_{10} t_p \) for the second pulse, and \( \gamma_i B_{10} t_p \) for the second pulse respectively. For these calculations, the two RF fields are applied orthogonally in the lab frame along the lab frame x and y axes. Detection is along the lab frame z-axis. The case labeled “0.414, 0.765, 0.765” corresponds to the situation which yields the largest echo for a properly oriented single crystal (i.e. \( \xi_1 = \pi/8, \xi_2 = \pi/4, \theta_1 = \theta_2 \) in eqns. (90) and (95)). It appears that this condition yields the largest echo for the powder sample as well.

Note that the phase, \( \varphi \), which appears in eqn (98) has the same effect as the phase shift seen in eqn (94). Hence, echo trains using \( \pm 90^o \) shifts for the refocusing pulse will be possible, just as is often done for the single frequency case. Here, only the sum of the phase shifts from the two RF sources matters, so the entire phase shift can be applied to just one of the RF sources.

When deriving eqn. (98), there are several terms not shown which could give rise to echos at times other than \( t = \tau \). The strength of those echos will depend on the nature of the quadrupole field distribution. For these secondary echos the echo times (in units of \( \tau \)) are determined by the
ratio of the various frequencies involved.
Figure 7 - echo amplitude for 2f measurement for a variety of conditions described in the text. All of these are calculated for $\eta = 0.5$.
Appendix A - Properties of Spin 1 Operators

Matrix Elements, Spin $I=1$, for energy eigenfunctions of the quadrupole Hamiltonian expressed in the principal axes system, where $|\pm\rangle$ and $|0\rangle$ are the usual eigenfunctions of $I_z$ -

$|\pm\rangle = (|1\rangle + |-1\rangle)/\sqrt{2}$

$|0\rangle = |0\rangle$

$\langle \pm | I_z |\pm\rangle = 0$

$\langle 0 | I_z |0\rangle = 0$

$\langle \pm | I_z |\mp\rangle = 1$

$\langle \pm | I_z |0\rangle = 0$

$\langle + | I_z |0\rangle = 1$

$\langle - | I_z |0\rangle = \pm 1$

$\langle \pm | I_{x,y} |\pm\rangle = 0$

$\langle 0 | I_{x,y} |0\rangle = 0$

$\langle + | I_{x} |0\rangle = 1$

$\langle + | I_{y} |0\rangle = 0$

$\langle - | I_{x} |0\rangle = 0$

$\langle - | I_{y} |0\rangle = -i$
Appendix A (con’t)

Matrix representations of operators (using +, -, and 0 basis functions in that order).

\[
I_z = \begin{pmatrix}
0 & 1 & 0 \\
1 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}, \quad
I_x = \begin{pmatrix}
0 & 0 & 1 \\
0 & 0 & 0 \\
1 & 0 & 0
\end{pmatrix}, \quad
I_y = \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & -i \\
i & 0 & 0
\end{pmatrix}
\]

\[
I_z^2 = \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 0
\end{pmatrix}, \quad
I_x^2 = \begin{pmatrix}
1 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 1
\end{pmatrix}, \quad
I_y^2 = \begin{pmatrix}
0 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

\[
I_z I_x = \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 1 \\
0 & 0 & 0
\end{pmatrix}, \quad
I_x I_z = \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 1 & 0
\end{pmatrix},
\]

\[
I_z I_y = \begin{pmatrix}
0 & 0 & -i \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}, \quad
I_y I_z = \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
i & 0 & 0
\end{pmatrix},
\]

\[
I_x I_y = \begin{pmatrix}
0 & i & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}, \quad
I_y I_x = \begin{pmatrix}
0 & -i & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix},
\]

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Appendix A (con’t)

Some relationships valid for $I = 1$.

\[ I_{\alpha}^{2n-1} = I_{\alpha} \quad \alpha = x, y, z; \ n = \text{integer, } n > 0 \]
\[ I_{\alpha}^{2n} = I_{\alpha}^2 \]

\[ e^{I_{\alpha}\theta} = (1 - I_{\alpha}^2) + I_{\alpha}^2 \cos \theta + i I_{\alpha} \sin \theta \]

\[ (I_x^2 - I_y^2)^{2n} = I_z^2 \quad ; \quad (I_x^2 - I_y^2)^{2n+1} = (I_x^2 - I_z^2) \quad n = \text{integer, } n > 0 \]
\[ (I_x^2 - I_z^2)^{2n} = I_y^2 \quad ; \quad (I_x^2 - I_z^2)^{2n+1} = (I_x^2 - I_y^2) \]
\[ (I_y^2 - I_z^2)^{2n} = I_x^2 \quad ; \quad (I_y^2 - I_z^2)^{2n+1} = (I_y^2 - I_x^2) \]

\[ \exp[i(I_x - I_y)\theta] = (1 - I_y^2) + I_y^2 \cos \theta + i(I_x^2 - I_y^2) \sin \theta \]
\[ \exp[i(I_x - I_z)\theta] = (1 - I_z^2) + I_z^2 \cos \theta + i(I_x^2 - I_z^2) \sin \theta \]
\[ \exp[i(I_y - I_z)\theta] = (1 - I_z^2) + I_z^2 \cos \theta + i(I_y^2 - I_z^2) \sin \theta \]

\[ [I_{\alpha}^2, I_{\beta}^2] = 0; \quad \alpha, \beta = x, y, z \]
Appendix B - Rotations of quadratic spin operators

1. Rotate by $\theta$ about the $z$-axis

\[
\begin{align*}
I_z^2 &\Rightarrow I_z^2 \\
I_x^2 &\Rightarrow I_x^2 \cos^2 \theta + I_y^2 \sin^2 \theta + \sin \theta \cos \theta (I_x I_y + I_y I_x) \\
I_y^2 &\Rightarrow I_y^2 \cos^2 \theta + I_z^2 \sin^2 \theta - \sin \theta \cos \theta (I_x I_y + I_y I_x) \\
I_x I_y &\Rightarrow I_x I_y \cos^2 \theta - I_y I_x \sin^2 \theta - \sin \theta \cos \theta (I_x^2 - I_y^2) \\
I_y I_x &\Rightarrow I_y I_x \cos^2 \theta - I_x I_y \sin^2 \theta - \sin \theta \cos \theta (I_y^2 - I_x^2) \\
I_y I_z &\Rightarrow I_y I_z \cos \theta - I_x I_z \sin \theta \\
I_z I_y &\Rightarrow I_z I_y \cos \theta - I_x I_z \sin \theta \\
I_z I_x &\Rightarrow I_z I_x \cos \theta + I_z I_y \sin \theta \\
I_x I_z &\Rightarrow I_x I_z \cos \theta + I_y I_z \sin \theta \\
(I_x^2 - I_y^2) &\Rightarrow (I_x^2 - I_y^2) \cos 2\theta + (I_x I_y + I_y I_x) \sin 2\theta \\
(I_x I_y + I_y I_x) &\Rightarrow (I_x I_y + I_y I_x) \cos 2\theta - (I_x^2 - I_y^2) \sin 2\theta \\
(I_y I_z + I_z I_y) &\Rightarrow (I_y I_z + I_z I_y) \cos \theta - (I_x I_z + I_z I_x) \sin \theta \\
(I_z I_x + I_x I_z) &\Rightarrow (I_z I_x + I_x I_z) \cos \theta + (I_y I_z + I_z I_y) \sin \theta \\
(I_x I_y - I_y I_x) &\Rightarrow (I_x I_y - I_y I_x) \\
(I_y I_z - I_z I_y) &\Rightarrow (I_y I_z - I_z I_y) \cos \theta + (I_z I_x - I_x I_z) \sin \theta \\
(I_z I_x - I_x I_z) &\Rightarrow (I_z I_x - I_x I_z) \cos \theta - (I_y I_z - I_z I_y) \sin \theta \\
\end{align*}
\]
2. Rotate by $\xi$ about the x-axis

\[
I_x^2 \Rightarrow I_x^2 \cos^2 \xi + I_y^2 \sin^2 \xi - \sin \xi \cos \xi (I_y I_x + I_z I_y)
\]

\[
I_x^2 \Rightarrow I_x^2
\]

\[
I_y^2 \Rightarrow I_y^2 \cos^2 \xi + I_z^2 \sin^2 \xi + \sin \xi \cos \xi (I_y I_z + I_z I_y)
\]

\[
I_x I_y \Rightarrow I_x I_y \cos \xi + I_y I_x \sin \xi
\]

\[
I_y I_x \Rightarrow I_y I_x \cos \xi + I_x I_y \sin \xi
\]

\[
I_y I_z \Rightarrow I_y I_z \cos^2 \xi - I_z I_y \sin^2 \xi - (I_y^2 - I_z^2) \sin \xi \cos \xi
\]

\[
I_z I_y \Rightarrow I_z I_y \cos^2 \xi - I_y I_z \sin^2 \xi - (I_y^2 - I_z^2) \sin \xi \cos \xi
\]

\[
I_x I_z \Rightarrow I_x I_z \cos \xi - I_z I_x \sin \xi
\]

\[
I_y I_z \Rightarrow I_y I_z \cos \xi - I_z I_y \sin \xi
\]

\[
(I_y^2 - I_z^2) \Rightarrow (I_y^2 - I_z^2) \cos 2\xi + (I_y I_z + I_z I_y) \sin 2\xi
\]

\[
(I_x I_y + I_y I_x) \Rightarrow (I_x I_y + I_y I_x) \cos \xi + (I_y I_x + I_x I_y) \sin \xi
\]

\[
(I_x I_z + I_z I_x) \Rightarrow (I_x I_z + I_z I_x) \cos 2\xi - (I_y^2 - I_z^2) \sin 2\xi
\]

\[
(I_z I_x + I_x I_z) \Rightarrow (I_z I_x + I_x I_z) \cos \xi - (I_y I_z + I_z I_y) \sin \xi
\]

\[
(I_x I_y - I_y I_x) \Rightarrow (I_x I_y - I_y I_x) \cos \xi - (I_z I_x - I_x I_z) \sin \xi
\]

\[
(I_y I_z - I_z I_y) \Rightarrow (I_y I_z - I_z I_y)
\]

\[
(I_z I_x - I_x I_z) \Rightarrow (I_z I_x - I_x I_z) \cos \xi - (I_y I_x - I_x I_y) \sin \xi
\]
3. Rotate by $\varphi$ about the y-axis

\[
\begin{align*}
I_z^2 & \Rightarrow I_z^2 \cos^2 \varphi + I_z^2 \sin^2 \varphi + \sin \varphi \cos \varphi (I_z I_x + I_x I_z) \\
I_x^2 & \Rightarrow I_x^2 \cos^2 \varphi + I_x^2 \sin^2 \varphi - \sin \varphi \cos \varphi (I_z I_x + I_x I_z) \\
I_y^2 & \Rightarrow I_y^2 \\
I_x I_y & \Rightarrow I_x I_y \cos \varphi - I_z I_y \sin \varphi \\
I_y I_x & \Rightarrow I_y I_x \cos \varphi - I_y I_z \sin \varphi \\
I_y I_z & \Rightarrow I_y I_z \cos \varphi + I_y I_x \sin \varphi \\
I_z I_y & \Rightarrow I_z I_y \cos \varphi + I_x I_y \sin \varphi \\
I_x I_z & \Rightarrow I_x I_z \cos^2 \varphi - I_x I_z \sin^2 \varphi - (I_x^2 - I_z^2) \sin \varphi \cos \varphi \\
I_x I_z & \Rightarrow I_x I_z \cos^2 \varphi - I_x I_z \sin^2 \varphi - (I_x^2 - I_z^2) \sin \varphi \cos \varphi \\
(I_x^2 - I_z^2) & \Rightarrow (I_x^2 - I_z^2) \cos 2\varphi + (I_x I_x + I_z I_z) \sin 2\varphi \\
(I_x I_y + I_y I_x) & \Rightarrow (I_x I_y + I_y I_x) \cos \varphi + (I_y I_z + I_z I_y) \sin \varphi \\
(I_y I_z + I_z I_y) & \Rightarrow (I_y I_z + I_z I_y) \cos \varphi + (I_x I_y + I_y I_x) \sin \varphi \\
(I_x I_x + I_z I_z) & \Rightarrow (I_x I_x + I_z I_z) \cos 2\varphi - (I_x^2 - I_z^2) \sin 2\varphi \\
(I_x I_y - I_y I_x) & \Rightarrow (I_x I_y - I_y I_x) \cos \varphi + (I_y I_z - I_z I_y) \sin \varphi \\
(I_y I_z - I_z I_y) & \Rightarrow (I_y I_z - I_z I_y) \cos \varphi - (I_x I_y - I_y I_x) \sin \varphi \\
(I_z I_x - I_x I_z) & \Rightarrow (I_z I_x - I_x I_z)
\end{align*}
\]
Appendix B (con’t)

4. The “2-f” rotation
(For simultaneous excitation at $\omega_x$ and $\omega_y$, with $B_1$’s of $B_{1x}$ and $B_{1y}$ respectively. $B_{1\text{eff}} = (B_{1x}^2 + B_{1y}^2)^{1/2}$, $\theta = \gamma B_{1\text{eff}} t_y/2$, $\cos\xi = B_{1y}/B_{1\text{eff}}$, $\sin\xi = B_{1x}/B_{1\text{eff}}$)

\[
I_z^2 \Rightarrow I_z^2 \left( \cos^2 \xi + \sin^2 \xi \cos \theta \right)^2
+ I_y^2 \cos^2 \xi \sin^2 \xi \left(1 - \cos \theta \right)^2
+ I_x^2 \sin^2 \xi \sin^2 \theta
+ \left( I_y I_x + I_x I_y \right) \sin \xi \cos \xi (\cos \theta - 1)(\cos^2 \xi + \sin^2 \xi \cos \theta)
+ \left( I_x I_y + I_y I_x \right) (- \sin \xi \sin \theta)(\cos^2 \xi + \sin^2 \xi \cos \theta)
+ \left( I_x I_y + I_y I_x \right) \sin^2 \xi \cos \xi \sin \theta (1 - \cos \theta)
\]

\[
I_x^2 \Rightarrow I_z^2 \sin^2 \theta \sin^2 \xi
+ I_y^2 \sin^2 \theta \cos^2 \xi
+ I_x^2 \cos^2 \theta
+ \left( I_y I_x + I_x I_y \right) \sin^2 \theta \sin \xi \cos \xi
+ \left( I_x I_y + I_y I_x \right) \sin \xi \sin \theta \cos \theta
+ \left( I_x I_y + I_y I_x \right) \sin \xi \sin \theta \cos \theta
\]

\[
I_y^2 \Rightarrow I_z^2 \sin^2 \xi \cos^2 \xi (1 - \cos \theta)^2
+ I_y^2 \left( \sin^2 \xi + \cos^2 \xi \cos \theta \right)^2
+ I_x^2 \cos^2 \xi \sin^2 \theta
+ \left( I_y I_x + I_x I_y \right) \sin \xi \cos \xi (\cos \theta - 1)(\sin^2 \xi + \cos^2 \xi \cos \theta)
+ \left( I_x I_x + I_x I_x \right) \cos^2 \xi \sin \xi \sin \theta (1 - \cos \theta)
+ \left( I_x I_y + I_y I_x \right) (- \cos \xi \sin \theta)(\sin^2 \xi + \cos^2 \xi \cos \theta)
\]

Con’t next page
Appendix B (con’t)
4. The “2f” rotation (con’t)

\[ I_y I_z \Rightarrow I_z^2 \sin^2 \xi \cos \xi (\cos \theta - 1)(\cos^2 \xi + \sin^2 \xi \cos \theta) \]
\[ + I_z^2 \sin^2 \xi \cos \xi (\cos \theta - 1)(\sin^2 \xi + \cos^2 \xi \cos \theta) \]
\[ + I_x^2 \sin \xi \cos \xi \sin^2 \theta \]
\[ + I_z I_x \sin^2 \xi \cos \xi \sin \theta (1 - \cos \theta) \]
\[ + I_x I_z (- \cos \xi \sin \theta)(\cos^2 \xi + \sin^2 \xi \cos \theta) \]
\[ + I_y I_z (\cos^2 \xi + \sin^2 \xi \cos \theta)(\sin^2 \xi + \cos^2 \xi \cos \theta) \]
\[ + I_z I_y \sin^2 \xi \cos^2 \xi (1 - \cos \theta)^2 \]
\[ + I_x I_y \sin \xi \cos \xi \sin \theta (1 - \cos \theta) \]
\[ + I_y I_x (- \sin \xi \sin \theta)(\sin^2 \xi + \cos^2 \xi \cos \theta) \]

(For \(I_y I_z\) reverse order of all operators - no change in geometric terms)

\[ I_z I_x \Rightarrow I_x^2 \sin^2 \xi \sin \theta (\cos^2 \xi + \sin^2 \xi \cos \theta) \]
\[ + I_x^2 \sin \xi \cos \xi \cos \theta (\cos \theta - 1) \]
\[ + I_z^2 (- \sin \xi \sin \theta \cos \theta) \]
\[ + I_y I_x \sin^2 \xi \cos \xi \sin \theta (\cos \theta - 1) \]
\[ + I_z I_y \cos \xi \sin \theta (\cos^2 \xi + \sin^2 \xi \cos \theta) \]
\[ + I_x I_y \cos \theta (\cos^2 \xi + \sin^2 \xi \cos \theta) \]
\[ + I_z I_x (- \sin^2 \xi \sin^2 \theta) \]
\[ + I_y I_x (- \sin \xi \cos \xi \sin^2 \theta) \]
\[ + I_y I_x \sin \xi \cos \xi \cos \theta (\cos \theta - 1) \]

(For \(I_x I_z\) reverse order of all operators - no change in geometric terms)

Con’t next page
4. The “2-f” rotation (con’t)

\[ I_x I_y \Rightarrow I_z^2 \sin^2 \xi \cos \xi \sin \theta (\cos \theta - 1) \]
\[ + I_y^2 \cos \xi \sin \theta (\sin^2 \xi + \cos^2 \xi \cos \theta) \]
\[ + I_x^2 (- \cos \xi \sin \theta \cos \theta) \]
\[ + I_z I_x (- \cos \xi \sin \xi \sin^2 \theta) \]
\[ + I_x I_z \cos \xi \sin \xi \cos \theta (\cos \theta - 1) \]
\[ + I_y I_z \cos^2 \xi \sin \xi \sin \theta (\cos \theta - 1) \]
\[ + I_z I_y \sin \xi \sin \theta (\sin^2 \xi + \cos^2 \xi \cos \theta) \]
\[ + I_x I_y \cos \theta (\sin^2 \xi + \cos^2 \xi \cos \theta) \]
\[ + I_y I_x (- \cos^2 \xi \sin^2 \theta) \]

(For \( I_y I_x \) reverse order of all operators - no change in geometric terms)
C. 2-f pulse, matrix representation

The results of two pulses simultaneously applied at $\omega_0$ and $\omega_1$ (eqn. (60)) can be written in matrix form. The wave function coefficients are written as a vector

$$|\psi\rangle = a|+\rangle + b|-\rangle + c|0\rangle \Rightarrow \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

and the result of the two frequency excitation is $R|\psi\rangle$, where in matrix form

$$R = \begin{pmatrix} \sin^2 \xi + \cos^2 \xi \cos \vartheta & ie^{-i\varphi} \cos \xi \sin \vartheta & ie^{-i(\varphi + \vartheta)} \sin \xi \cos \xi (1 - \cos \vartheta) \\ ie^{i\varphi} \cos \xi \sin \vartheta & \cos \vartheta & e^{-i\varphi} \sin \xi \sin \vartheta \\ -ie^{i(\varphi + \vartheta)} \sin \xi \cos \xi (1 - \cos \vartheta) & e^{i\varphi} \sin \xi \sin \vartheta & \cos^2 \xi + \sin^2 \xi \cos \vartheta \end{pmatrix}$$

where $\vartheta = \omega_{\text{eff}}/2$ and $\cos \xi = \omega_1/\omega_{\text{eff}}$ and $\sin \xi = \omega_1/\omega_{\text{eff}}$. 

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## Appendix D

Typical $^{14}$N NQR Frequencies

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$e^2qQ/h$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inorganic Nitrates</td>
<td>470-800 kHz</td>
</tr>
<tr>
<td>Substituted Nitrobenzenes</td>
<td>0.9-1.5</td>
</tr>
<tr>
<td>Anilines</td>
<td>3.9-4.1</td>
</tr>
<tr>
<td>Organic Nitriles</td>
<td>3.7-4.2</td>
</tr>
<tr>
<td>Substituted Pyridines</td>
<td>4.3-4.81</td>
</tr>
<tr>
<td>Azabenzenes</td>
<td>4.4-5.2</td>
</tr>
</tbody>
</table>

See: