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Multipole NMR. VI. Application to Coherence Transfer and 2-D Spectroscopy in a Spin-1 System

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Using the multipole formulation the recent experiments of H. Hatanaka and C. S. Yannoni (*J. Magn. Reson.* 42, 330 (1981)) are interpreted. It is shown how transfer of nuclear coherence between levels in a spin-1 system corresponds to a transfer of polarization between single quantum dipole character and single quantum quadrupole character. Also discussed in the multipole formulation are the recent experiments of L. Müller (*J. Magn. Reson.* 42, 324 (1981)) in which 2-D spectroscopy is used to extract the double quantum spectrum. Some comments are made regarding a spin $I = \frac{3}{2}$.

I. INTRODUCTION

In a recent paper by Hatanaka and Yannoni (*1*) experiments are described in which nuclear coherence is selectively created by the use of nonselective pulses on a spin 1 system. This experiment nicely illustrates earlier discussions regarding the use of selective and nonselective pulse sequences to excite selectivity multiquantum coherences. In particular it is argued (*2*) that pure (δ-function, hard) pulses, when experimentally possible, have considerable advantage over selective (nonpure, weak) pulses, since the former excite only a few polarizations while the latter, on account of internal interactions, tend to distribute the polarization into modes not coupled by the rf field. This means the mathematical complications drastically increase in moving from pure to nonpure pulse sequences as well as spoiling the simple picture of rotation of a polarization subject to pure pulses. Furthermore, to understand multiquantum processes, echo formation, and 2-D spectroscopy (*3*) it is imperative to have a mathematical framework which permits the time evolution of the polarizations to be followed as they respond to pulse–delay sequences. To try to visualize this, various authors have devised multiple coordinate frames in which the spin operators evolve (*4*). Although these have provided very useful pictures in specific cases ($I = 1$), it is a human limitation that visualization of processes in coordinate frames with more than three dimensions is difficult. It is essential, however, for spins greater than $\frac{1}{2}$ that the vector model be extended to include other polarizations, i.e., higher multipoles. To describe spin polarizations the multipoles are organized into tensors which are invariants to rotations in 3-dimensional space (*5–7*). Apart from the usual spherical basis no other coordinate frame is introduced.

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The use of nuclear multipoles can be directly compared to the use of spherical harmonics as atomic orbitals. Just as the electrostatic interactions lead to a LCAO, so the nuclear Hamiltonian leads to a linear combination of multipole polarizations (*8*) (LCMP).

The goal of this paper is to use the multipole approach to describe the particular coherence transfer experiments of Hatanaka (*1*) and the double quantum spectrum of Müller (*3*). These examples are considered typical of systems of noninteracting spins subject to an electric quadrupole interaction. No distinction is made here between an equivalent pair of dipolar coupled spins of ½ such as the fluorine pair (*1*) and the deuterium ($I = 1$) used in the experiments, (*3*) both being treated as a spin 1.

This paper rests upon earlier work on the multipole approach. Paper I (*9*) treats theoretical aspects of multispin multipole operators while paper II (*10*) includes relaxation effects. Paper III (*11*) compares the multipole formulation for single spins with the fictitious spin-½ approach. Paper IV (*8*) solves the single spin problem with an electric quadrupole interaction and treats effects of pure pulses, leading to the analysis of multiquantum production and evolution for pulse sequences. Paper V (*2*) treats pure pulses, selective pulses, and nonselective pulses on a single spin system.

These works, as well as the present, make use of the idea of multipole character of a multiquantum spectrum. The maximum multipole character corresponds to $k = 2I$, meaning spin ½ has $k = 1$, dipole character; spin 1 has dipole, $k = 1$, and quadrupole, $k = 2$, character; spin ⅜ has in addition octupole, $k = 3$, character and so forth. Each multipole has $2k + 1$ components q which, in the spherical basis used, correspond to the order of the spin transition, $q = \Delta M$. For single spins, $q = \Delta M \neq 0$ correspond to coherences, i.e., single quantum $q = \pm 1$, double quantum, $q = \pm 2$. For $q = 0$, the single spin operator describes an incoherent superposition of states, although for multispin systems, coherent effects can occur for $q = 0$. Each multipole component is described by a multipole operator $\mathcal{T}^{(k)q}(\mathbf{I})$ which displays the multipole character k and spherical component q. Each has a representation in the $(2I + 1)^2$ spin space, but the important properties have to do with the rotational transformations of the $\mathcal{T}^{(k)q}(\mathbf{I})$ (*9*, *11*) which, in the classical limit, become proportional to spherical harmonics Y_{kq}. The $\mathcal{T}^{(k)q}$ form a complete orthonormal operator basis, therefore any spin operator can be written in the multipole basis. In particular, the spin density operator is (*11*)

$$\sigma_1(t) = \frac{1}{2I + 1}\left[E_1 + \sum_{k=1}^{2I}\sum_{q=-k}^{k} \phi_q^k(t)\mathcal{T}^{(k)q}(\mathbf{I})\right] \qquad [1]$$

where E_1 is the identity. The $\phi_q^k(t)$ describe the multipole polarizations and the set of polarizations describe the multipole character of the spin system.

Using the orthogonality of the $\mathcal{T}^{(k)q}(\mathbf{I})$ (*11*), the polarizations are seen to be quantum averages of their corresponding multipole operators,

$$\phi_q^k(t) = \text{Trace}\{\sigma_1(t)\mathcal{T}_q^{(k)}\} = \langle \mathcal{T}_q^{(k)} \rangle \qquad [2]$$

where $\mathcal{T}^{(k)q^\dagger} = \mathcal{T}_q^{(k)} = (-1)^{k-q}\mathcal{T}^{(k)-q}$. Since the NMR experiment detects only the xy

component of the nuclear magnetization, only $\phi^1_{\pm 1}$ is physically observable (*8*), giving the average dipole moment as

$$\langle \mu^1_{\pm 1} \rangle \alpha \phi^1_{\pm 1}(t) = \pm \frac{i}{\sqrt{2}} (\phi_x \mp i\phi_y). \qquad [3]$$

The higher multipoles, $k > 1$, and other coherences $q \neq 1$ can affect the observable magnetization and must in many cases be calculated even if they are not directly observed.

To show the effects of multipole character, consider Fig. 1, which shows the single quantum multipole character for $I = 1$ and the single and double quantum multipole character for $I = 3/2$. For $I = 1$, the double quantum and for $I = 3/2$, the triple quantum coherences have only one frequency and are not shown. The intensity and relative sense (positive or negative) of each multipole contribution is easily found from the MM' representation of each $\mathcal{Y}^{(k)q}$. These change with I for a given kq and are listed in Table I of Paper III (*11*) for $I \leqslant 5/2$. For reference here the complete set of $\mathcal{Y}^{(k)q}$ are given for $I = 1$,

$$\mathcal{Y}^{(1)0}(\mathbf{I}) = i\sqrt{\frac{3}{2}} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \qquad [4]$$

$$\mathcal{Y}^{(1)1}(\mathbf{I}) = -i\sqrt{\frac{3}{2}} \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{bmatrix} \qquad [5]$$

$$\mathcal{Y}^{(2)0}(\mathbf{I}) = \frac{1}{\sqrt{2}} \begin{bmatrix} -1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & -1 \end{bmatrix} \qquad [6]$$

$$\mathcal{Y}^{(2)1}(\mathbf{I}) = \sqrt{\frac{3}{2}} \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & -1 \\ 0 & 0 & 0 \end{bmatrix} \qquad [7]$$

$$\mathcal{Y}^{(2)2}(\mathbf{I}) = \sqrt{3} \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}. \qquad [8]$$

For $I = 3/2$, only the single quantum operators, $q = 1$

$$\mathcal{Y}^{(1)1}(\mathbf{I}) = -i\sqrt{\frac{6}{5}} \begin{bmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 2/\sqrt{3} & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{bmatrix} \qquad [9]$$

$$\mathcal{Y}^{(2)1}(\mathbf{I}) = -\sqrt{2} \begin{bmatrix} 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{bmatrix} \qquad [10]$$

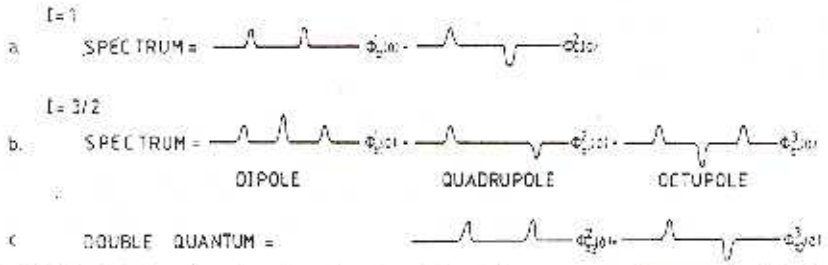

FIG. 1. (a) The dipole and quadrupole character of the single quantum coherences for $I = 1$. (b) The dipole, quadrupole, and octupole character of the single quantum coherences. (c) The quadrupole and octupole double quantum coherences for a spin $I = 3/2$.

$$\mathcal{I}^{(3)1}(\mathbf{I}) = \frac{i2}{\sqrt{5}} \begin{bmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & -\sqrt{3} & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{bmatrix} \qquad [11]$$

and the double quantum coherences, $q = 2$

$$\mathcal{I}^{(2)2}(\mathbf{I}) = -\sqrt{2} \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \qquad [12]$$

and

$$\mathcal{I}^{(3)2}(\mathbf{I}) = i\sqrt{2} \begin{bmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \qquad [13]$$

are given for comparison with Fig. 1.

The single quantum modes $q = \pm 1$ all lie one-off the diagonal, the double, $q = \pm 2$, are two-off the diagonal, etc. Each multipole operator makes a unique contribution to the spectrum if it has been polarized by a previous preparation, i.e., if the $\phi_q^k(0)$ in Fig. 1 are nonzero. Varying the $\phi_q^k(0)$ from one experiment to the next will result in a change in the spectral intensity as the multipole character is varied. Two-dimensional spectroscopy (*12*) makes use of systematic variations in single quantum spectral intensities to extract information about higher multipoles which are not directly observable.

The experiments of Hatanaka and Yannoni (*1*) can be readily understood in terms of the mixing of multipole character. In their experiment on a strongly coupled pair of fluorines, they are able to transfer coherence from the normal doublet, to only one line, Fig. 2. For this quasi-spin-1 system the sequence they use,

$$(\pi/4)_y - \tau_1 - (\pi/2)_x - \tau_2 \qquad [14]$$

creates equal parts of dipole, $\phi_{\pm 1}^1$, and quadrupole, $\phi_{\pm 1}^2$, single quantum coherences. In the FID, the τ_2 period following the second pulse, one line is enhanced while the

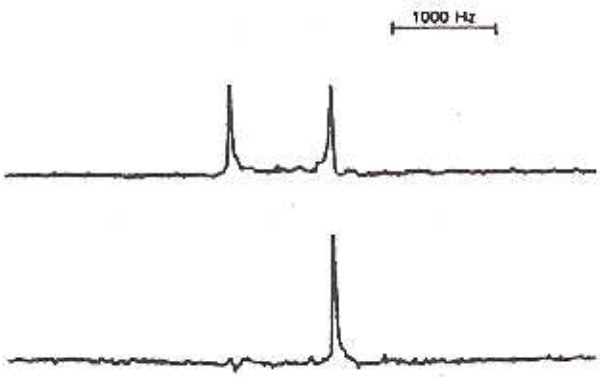

FIG. 2. From Fig. 1 of Ref. (*1*). Selective creation of coherence using a nonselective pulse sequence. The upper trace is the normal spectrum of fluorine nuclei of 1,1-difluorotetrachloroethane in a nematic liquid crystal solvent. The lower trace shows that one resonance line disappears after the pulse sequence $(\pi/4)_y - \tau - (\pi/2)_x$ and the remaining line is enhanced by $2^{1/2}$.

other cancels. Changing the rf phase of the second pulse by 180° to $-x$ reverses the enhancement cancellation. It is observed, moreover, that the sequence, Eq. [14], enhances the intensity over the usual single $(\pi/2)_y$ pulsed FT-FID spectrum by a factor of $\sqrt{2}$.

Qualitatively it is easily seen at a glance from Fig. 1 how the multipole character accounts for this behavior. The three pulse sequence used by Müller (*3*) to obtain the double quantum spectrum of deuterium also has a simple interpretation in terms of multipoles. The next three sections treat these effects quantitatively.

II. THEORY

The evolution of spin 1 from an equilibrium dipole polarization lying along the z axis is described by a series of transformations. The effect of a pure rf pulse applied on a time scale which is fast enough to ignore internal couplings is described by the Hamiltonian (*8*),

$$\mathscr{H}_{rf} = -\gamma\hbar H_0 I_z + \gamma\hbar H_1 \cos(\omega t - \phi) I_x - \gamma\hbar H_1 \sin(\omega t - \phi) I_y \qquad [15]$$

where ϕ is an arbitrary phase angle defined relative to the positive (*8*) x axis. The effect of a resonance pulse is given by a rotation (*6*),

$$\hat{\phi}_\phi^k[(\beta)_\phi] = \sum_q \mathscr{D}_{qq}^{(k)}\left(-\left(\phi - \frac{\pi}{2}\right)\beta\left(\phi - \frac{\pi}{2}\right)\right)\phi_q^k(0) \qquad [16]$$

where $\beta = \omega_1\tau$, $\omega_1 = \gamma H_1$, and τ is the duration of the pulse. It is assumed that the initial equilibrium magnetization lies along the z axis normalized to $\phi_0^1(0) = -i$ (*8*).

When the *rf* pulse is off, the system evolves under the nuclear electronic quadrupole interaction given by (*8*)

$$\mathscr{H} = -\gamma\hbar H_0 I_z + \frac{\hbar\tilde{Q}}{2}\{3I_z^2 - I(I+1)\} = i\hbar\omega_0 \sqrt{\frac{2}{3}}\, \mathscr{V}^{(1)0}(\mathbf{I}) - \frac{\hbar\tilde{Q}}{2}\mathscr{V}^{(2)0}(\mathbf{I}). \qquad [17]$$

The time evolution resulting from this Hamiltonian is (*8*)

$$\tilde{\phi}^k_0(t) = \tilde{\phi}^k_0(0) \qquad [18]$$

$$\tilde{\phi}^2_{-1}(t) = \tilde{\phi}^2_{-1}(0) \qquad [19]$$

and

$$\begin{bmatrix} \tilde{\phi}^1_{\pm 1}(t) \\ \tilde{\phi}^2_{\pm 1}(t) \end{bmatrix} = \begin{bmatrix} \cos\dfrac{3\tilde{Q}t}{2} & \pm\sin\dfrac{3\tilde{Q}t}{2} \\ \mp\sin\dfrac{3\tilde{Q}t}{2} & \cos\dfrac{3\tilde{Q}t}{2} \end{bmatrix} \begin{bmatrix} \tilde{\phi}^1_{\pm 1}(0) \\ \tilde{\phi}^2_{\pm 1}(0) \end{bmatrix} \qquad [20]$$

valid for $I = 1$. The derivation of Eq. [20] is straightforward using any method, i.e., multipoles, fictitious spin (*13*), $|IM\rangle$ bases, etc. The multipole approach, however, enables the analytic solution to be found for any I of interest by a simple calculation. Reference (*2*) gives the general equation valid for all I and solves them for $I \leq \frac{9}{2}$.

In the above equations, the rotating frame is defined by the Larmor frequency, $\omega_0 = \gamma H_0$

$$\tilde{\phi}^k_q \equiv \exp[-iq\omega_0 t]\phi^k_q \,. \qquad [21]$$

Clearly from Eqs. [18]–[20], only the single quantum modes, $\tilde{\phi}^1_{\pm 1}$ and $\tilde{\phi}^2_{\pm 1}$ are not constants of the motion in the rotating frame.

Equations [16] and [18]–[20] enable the response of the spin density matrix to be calculated for the pulse sequence Eq. [14].

III. COHERENCE TRANSFER

From Ref. (*1*), the Hamiltonian for the free evolution is given by

$$\begin{aligned} \mathscr{H}/h &= \delta I'_z = \frac{\delta}{3}\,|Q_{-1}(ab) - Q_{-1}(bc)| \\ &= \frac{\delta}{3}\,[|a\rangle\langle a| + |c\rangle\langle c| - 2|b\rangle\langle b|] = -\frac{\delta\sqrt{2}}{3}\,\mathscr{T}^{(20)}(\mathrm{I}). \end{aligned} \qquad [22]$$

The notation $I'_z Q_{-1}(\mathrm{ij})$ is given in Ref. (*1*) while $|a\rangle$, $|b\rangle$, and $|c\rangle$ refer to the three levels of a spin 1. $\mathscr{T}^{(20)}$ is identified from Eq. [6]. It is obvious that the dipolar coupled fluorine pair can be treated as a quasi-spin-1 particle subject to a pseudoquadrupole interaction. From Eq. [17], δ is identified as

$$\delta = \tfrac{3}{2}\tilde{Q} \qquad [23]$$

In Paper IV (*8*) the effects of pulse sequences starting from an initial $(\pi/2)$ pulse are described. For $I = 1$, the FID following such a pulse is given by (*8*)

$$\tilde{\phi}^1_{\pm 1}[(\pi/2)_{\phi_1} - \tau_1] = \frac{e^{\mp i\phi_1}}{\sqrt{2}}\cos\delta\tau_1 \,. \qquad [24]$$

Clearly in the rotating frame, the magnetization oscillates with two frequencies, $\pm\delta$. Fourier transforming Eq. [24] gives the two lines in Fig. 2, with normalized intensity of $1/(2\sqrt{2})$.

Not observable, and oscillating out of phase with $\hat{\phi}^1_{\pm 1}$ are the quadrupole single quantum components,

$$\hat{\phi}^2_{\pm 1}[(\pi/2)_{\phi_1}-\tau_1] = \mp \frac{e^{\mp i\phi_1}}{\sqrt{2}} \sin \delta\tau_1. \quad [25]$$

If τ_1 is chosen to be $n\pi/(2\delta)$, for integer n, then all the dipole character is converted to quadrupole character. The pulse sequence (8) $(\pi/2)_{\phi_1}-\tau_1-(\beta_2)_{\phi_2}-\tau_2$ for $I = 1$ is discussed in Paper IV (8). The polarizations with dipole and quadrupole character produced by an initial $(\pi/2)_0$ pulse, however, cannot be mixed by any second pulse $(\beta_2)_{\phi_2}$ (8) so as to cause the enhancement-cancellation effect observed by Hatanaka and Yannoni (1). It can only be done if the initial pulse is a $(\pi/4)_0$ pulse. The effect of this pulse is found by straightforward application of Eq. (16) to give

$$\hat{\phi}^1_{\pm 1}[(\pi/4)_0] = 1/2 \quad [26]$$

$$\hat{\phi}^1_0[(\pi/4)_0] = \frac{-i}{\sqrt{2}}. \quad [27]$$

In other words a $\pi/4$ pulse produces some single quantum dipole coherence, but, as expected, leaves some polarization in the z direction ($\hat{\phi}^1_0 \neq 0$) which remains constant on a time scale short with respect to T_1. The single quantum coherences evolve according to Eq. [20] with initial conditions $\hat{\phi}^1_{\pm 1} = 1/2$ and $\hat{\phi}^2_{\pm 1} = 0$ giving

$$\hat{\phi}^1_{\pm 1}[(\pi/4)_0-\tau_1] = 1/2 \cos \delta\tau_1 \quad [28]$$

$$\phi^2_{\pm 1}[(\pi/4)_0-\tau_1] = \mp 1/2 \sin \delta\tau_1. \quad [29]$$

Before the second pulse is applied (on a time scale short with respect to T_2), τ_1 is chosen, in agreement with experiment as $\tau_1 = \pi/(2\delta)$ so $\delta\tau_1 = \pi/2$, or

$$\hat{\phi}^1_{\pm 1}[(\pi/4)_0-\tau_1] = 0 \quad [30]$$

$$\hat{\phi}^2_{\pm 1}[(\pi/4)_0-\tau_1] = \mp 1/2. \quad [31]$$

Clearly the second $\pi/2$ pulse acts on a spin system which contains only quadrupole single quantum coherence, $\hat{\phi}^2_{\pm 1} = \mp 1/2$ and residual z magnetization, Eq. [27], $\hat{\phi}^1_0 = -i\sqrt{2}$. The second $(\pi/2)_{\phi_2}$ pulse applied at phase angle ϕ_2 gives single quantum coherence with both dipole character

$$\hat{\phi}^1_{\pm 1}[(\pi/4)_0-\tau_1-(\pi/2)_{\phi_2}] = 1/2 e^{\mp i\phi_2} \quad [32]$$

and quadrupole character,

$$\hat{\phi}^2_{\pm 1}[(\pi/4)_0-\tau_1-(\pi/2)_{\phi_2}] = \frac{i}{2} e^{\mp i\phi_2} \sin \phi_2 \quad [33]$$

both obtained from knowledge of the rotation matrix elements (6) $\mathcal{D}^{(k)}_{qq'}(-(\phi - \pi/2)\pi/2(\phi - \pi/2))$, $k = 1, 2$.

These now comprise the initial conditions in Eq. [20] for the final evolution resulting in a detectable polarization of

$$\hat{\phi}^1_{\pm 1}[(\pi/4)_0-\tau_1-(\pi/2)_{\phi_2}-\tau_2] = \frac{e^{\mp i\omega_1}}{2} [\cos \delta\tau_2 \pm i \sin \phi_2 \sin \delta\tau_2]. \quad [34]$$

If the phase is chosen to be $\phi_2 = 0, \pi, 2\pi$, etc., then FT-FID gives two lines similar to Fig. 2, but with a relative intensity of ¼. On the other hand, a phase of $\phi_2 = -\pi/2$ as used in reference (*1*) leads to only one frequency,

$$\hat{\phi}^1_{\pm 1}[(\pi/4)_0\text{-}\tau_1\text{-}(\pi/2)_{-\pi/2}\text{-}\tau_2] = \pm \frac{i}{2} \exp(\mp i\delta\tau_2). \quad [35]$$

Using Eq. [3], the commonly detected x and y components of the magnetization obey

$$\hat{\phi}_x = \tfrac{1}{2} \cos \delta\tau_2 \quad [36]$$

$$\hat{\phi}_y = \tfrac{1}{2} \sin \delta\tau_2 \quad [37]$$

corresponding to a single frequency in the rotating frame in agreement with Fig. [2]. From Eq. [35] the relative intensity of the spectrum obtained by complex Fourier transformation of the quadrature-detected FIDs is given by ½ which is an enhancement over the $(\pi/2)_0$ pulse-FID, Eq. [24], result by $\sqrt{2}$. Moreover, if the second pulse is phase shifted by 180° to $\phi_2 = +\pi/2$, the sign of the precession change to $-\delta$ corresponding to a transfer of coherence to the other line of Fig. 2. Finally for $\phi_2 = -\pi/2$, if the rotating frame is changed from ω_0 to $\omega_0 + \delta$ in Eq. [21] then

$$\hat{\phi}^1_{\pm 1}[(\pi/4)_0\text{-}\tau_1\text{-}(\pi/2)_{-\pi/2}\text{-}\tau_2] = \pm \frac{i}{2}. \quad [38]$$

In this frame the magnetization is constant. Changing the rf phase angle to $\phi_2 = \pi/2$ in the $\omega_0 + \delta$ frame causes the magnetization to precess "off-resonance" at 2δ, but would be constant in a rotating frame of $\omega_0 - \delta$.

All these consequences are in complete agreement with the observed results (*1*).

IV. DOUBLE QUANTUM SPECTRUM

The D NMR experiments on a polycrystalline sample of 28%-D ferrocene described in Ref. (*3*) point out a number of compelling reasons for studying double quantum spectra. The technique combines double-quantum NMR with magic-angle spinning. The theoretical analysis in that paper uses the Heisenberg picture to calculate the density operator for a spin 1 subject to the pulse sequence,

$$(\pi/2)_0\text{-}\tau_1\text{-}(\pi/2)_0\text{-}\tau_2\text{-}(\pi/2)_0\text{-}\tau_3. \quad [39]$$

The treatment (*3*) retains the finite time of the pulses t_p which with the pure-pulse approach used here (*8*) takes $t_p = 0$. Apart from this difference the results of Ref. (*3*) and that presented here agree. The point of the calculation given here is to show the consequences of the multipole formulation.

As has been noted before (*12*) a $\gamma_{12} = (\pi/2)_0\text{-}\tau_1\text{-}(\pi/2)_0\text{-}\tau_2$ pulse sequence on a spin 1 produces only so-called Zeeman order and double quantum polarization. In

the language of the multipole formulation after the $\pi/2$ phase unshifted pulse pair, of the 8 polarizations possible for a spin 1, the only nonzero polarizations are ($\chi_1 = \frac{3}{2}Q\tau_1 = \delta\tau_1$) (*8*)

$$\tilde{\phi}_0^1[\gamma_{12}] = i \cos \chi_1 \qquad [40]$$

$$\tilde{\phi}_{\pm 2}^2[\gamma_{12}] = \mp \frac{i}{2} \sin \chi_1 \qquad [41]$$

with $\tilde{\phi}_{\pm 1}^1[\gamma_{12}] = \tilde{\phi}_{\pm 1}^2[\gamma_{12}] = \tilde{\phi}_0^2[\gamma_{12}] = 0$. This means that in the τ_2 period after the second pulse no magnetization is detectable since $\tilde{\phi}_{\pm 1}^1[\gamma] = 0$. In the laboratory frame, however, there is a nondetectable evolution taking place, namely the double quantum coherence with time dependence given by

$$\phi_{\pm 2}^2[\gamma_{12}] = \mp \frac{i}{\sqrt{2}} \sin \chi_1 e^{\mp i 2\omega_0 \tau_2}. \qquad [42]$$

The goal of 2-D spectroscopy is to detect this double quantum coherence which is done by the application of a third pulse to put $\phi_{\pm 2}^2[\gamma]$ into single quantum detectable modes.

To compare with the treatment of Ref. (*3*) we introduced a small nonresonance part which may be present in the system and require $|\Delta\omega| \ll \omega_1$ where $\Delta\omega = \omega - \omega_0$. In the ω rotating frame, Eq. [42] becomes

$$\phi_{\pm 2}^2[\gamma_{12}] = \mp \frac{i}{\sqrt{2}} \sin \chi_1 e^{\mp i 2\Delta\omega\tau_2} \qquad [43]$$

showing that the duration of the time period τ_2 before the application of the third pulse leads to a pure double quantum oscillation of $\phi_{\pm 2}^2[\gamma_{12}]$ while $\phi_0^1[\gamma_{12}]$ is constant and all other polarizations are zero. Hence, by applying the third pulse at varying times τ_2, varying amounts of $\phi_{\pm 2}^2[\gamma_{12}]$ are produced oscillating at the double quantum frequency in the laboratory frame. The third $(\pi/2)_{\phi_3}$ pulse puts all the Zeeman polarizations ϕ_0^1 into single quantum modes with dipole character,

$$\phi_{\pm 1}^1[\gamma_{123}] = -\frac{e^{\mp i\phi_3}}{\sqrt{2}} \cos \chi_1 \qquad [44]$$

while the double quantum mode is put in part into single quantum modes with quadrupole character (*8*)

$$\phi_{\pm 1}^2[\gamma_{123}] = \pm e^{\mp i\phi_3} \sin \chi_1 e^{\mp i 2\Delta\omega\tau_2} \cos 2\phi_3 \qquad [45]$$

where $\gamma_{123} = \gamma_{12} - (\pi/2)_{\phi_3}$. In this example, relaxation is ignored but can be included empirically.

Equations [44] and [45] now form the initial condition for the final evolution in period τ_3 according to Eq. [20] giving

$$\tilde{\phi}_{\pm 1}^1[(\pi/2)_0 - \tau_1 - (\pi/2)_0 - \tau_2 - (\pi/2)_{\phi_3} - \tau_3]$$

$$= -\frac{e^{\mp i\phi_3}}{\sqrt{2}} [\cos \chi_1 \cos \chi_3 - \cos 2\phi_3 \sin \chi_1 \sin \chi_3 e^{\mp i 2\Delta\omega\tau_2}]. \qquad [46]$$

Using Eq. [3] this result reduces to the special cases of Eqs. [7a] and [7b] in Ref. (*3*). The identities

$$\cos(\chi_1)\cos(\chi_2) = \tfrac{1}{2}[\cos(\chi_1 - \chi_2) + \cos(\chi_1 + \chi_2)] \qquad [47]$$

and

$$\sin(\chi_1)\sin(\chi_2) = \tfrac{1}{2}[\cos(\chi_1 - \chi_2) - \cos(\chi_1 + \chi_2)] \qquad [48]$$

show both terms in Eq. [46] produce echoes at $\tau_3 = \tau_1$ when the cosine argument is zero.

The first term of Eq. [46] is referred to as a Zeeman echo and is present for any phase ϕ_3. It can vary with τ_1 and can be made to vanish if $\chi_1 = \pi/2$ as in the coherence transfer case of the previous section. For polycrystalline samples this corresponds to applying the second pulse at the maximum slope of the FID (*14*).

The second term also produces an echo at $\tau_3 = \tau_1$, called the double quantum echo (*3*). The amplitude can be modulated by varying the length of the τ_2 period. Fourier transforming the echo intensity with respect of τ_2 produces the double quantum spectrum, as shown experimentally in Ref. (*3*).

V. DISCUSSION

The explanation of the coherence transfer experiments of Hatanaka and Yannoni (*1*) has a very simple qualitative and quantitative interpretation when viewed in terms of nuclear multipoles and multipole character. Essential to the experiment is the initial $(\pi/4)_0$ pulse which partitions the magnetization between the z direction and the xy direction. The former is unchanged in the τ_1 period which, chosen as $\delta\tau_1 = \pi/2$, transfers all the latter to single quantum coherence with quadrupole character. The final $(\pi/2)_{\phi_2}$–τ_2 part mixes the zero quantum $\hat{\phi}_0^1$ and single quantum, $\hat{\phi}_{\pm 1}^2$, coherence according to Eq. [34] in complete agreement with observation (*1*).

It is remarked that coherence transfers should be possible for spin systems with $I > 1$ similar to the results discussed here. For reference the magnetization for $I = 1$ and $I = \frac{3}{2}$ are given for initial $\pi/2$ and $\pi/4$ pulses:

$$I = 1\text{: } (\chi_i = \tfrac{3}{2}\tilde{Q}\tau_i = \delta\tau_i).$$

$$\hat{\phi}_{\pm 1}^1[(\pi/2)_0\text{–}\tau_1\text{–}(\beta_2)_{\phi_2}\text{–}\tau_2] = \frac{e^{\mp i\phi_2}}{\sqrt{2}}\{\cos\phi_2\cos\beta_2\cos(\chi_1 + \chi_2) \pm i\sin\phi_2[\cos\chi_1\cos\chi_2 - \sin\chi_1\sin\chi_2(2\cos^2\beta_2 - 1)]\}. \qquad [49]$$

$$\hat{\phi}_{\pm 1}^1[(\pi/4)_0\text{–}\tau_1\text{–}(\beta_2)_{\phi_2}\text{–}\tau_2] = \tfrac{1}{2}e^{\mp i\phi_2}\sin\beta_2\cos\chi_2 + \frac{1}{\sqrt{2}}\hat{\phi}_{\pm 1}^1[(\pi/2)_0\text{–}\tau_1\text{–}(\beta_2)_{\phi_2}\text{–}\tau_2]. \qquad [50]$$

$$I = \tfrac{3}{2}\text{: } (\chi_i = \tilde{Q}\tau_i).$$

$$\hat{\phi}_{\pm 1}^1[\gamma_i - \tau_3] = \tfrac{1}{5}(2 + 3\cos\chi_2)\hat{\phi}_{\pm 1}^1(\gamma_i) \pm \sqrt{\frac{3}{5}}\sin\chi_2\hat{\phi}_{\pm 1}^2(\gamma_i) + \frac{\sqrt{6}}{5}(1 - \cos\chi_2)\hat{\phi}_{\pm 1}^3(\gamma_i). \qquad [51]$$

where for $\gamma_1 = (\pi/2)_0\text{-}\tau_1\text{-}(\beta_2)_{\phi_2}$,

$$\tilde{\phi}^1_{\pm 1}(\gamma_1) = \frac{e^{\mp i\phi_2}}{\sqrt{25}}(2 + 3\cos\chi_1)(\cos\beta_2\cos\phi_2 \pm i\sin\phi_2), \quad [52]$$

$$\tilde{\phi}^2_{\pm 1}(\gamma_1) = \mp\sqrt{\frac{3}{10}}\, e^{\mp i\phi_2}\sin\chi_1[\cos\beta_1\cos\phi_2 \pm i\sin\phi_2(2\cos^2\beta_2 - 1)], \quad [53]$$

$$\tilde{\phi}^3_{\pm 1}(\gamma_1) = \frac{\sqrt{3}}{20}\, e^{\mp i\phi_2}(1 - \cos\chi_1)[15\cos^3\beta_2 - 11\cos\beta_2)\cos\phi_2 \pm i(5\cos^2\beta_2 - 1)\sin\phi_2], \quad [54]$$

and for $\gamma_2 = (\pi/4)_0\text{-}\tau_1\text{-}(\beta_2)_{\phi_2}$,

$$\tilde{\phi}^1_{\pm 1}(\gamma_2) = \tfrac{1}{2}e^{\mp i\phi_2}\sin\beta_2 + \frac{1}{\sqrt{2}}\tilde{\phi}^1_{\pm 1}(\gamma_1), \quad [55]$$

$$\tilde{\phi}^2_{\pm 1}(\gamma_2) = \frac{1}{\sqrt{2}}\tilde{\phi}^2_{\pm 1}(\gamma_1), \quad [56]$$

$$\tilde{\phi}^3_{\pm 1}(\gamma_2) = \frac{1}{\sqrt{2}}\tilde{\phi}^3_{\pm 1}(\gamma_1). \quad [57]$$

Equation [34] is a special case of Eq. [50]. For $I = \frac{3}{2}$ a variety of coherence enhancement cancellations are possible. For example the sequence $(\pi/2)_0\text{-}\tau_1\text{-}(\beta_2)_0\text{-}\tau_2$ produces no central line when $\cos\beta_2 = \sqrt{5}/3$. It remains to experimentally test Eqs. [51]–[57] for a spin $\frac{3}{2}$.

For the triple pulse sequence used for the double quantum spectrum discussed in Section IV the effect of the first two inphase $\pi/2$ pulses is given by Eq. [49]. Clearly $\tilde{\phi}^1_{\pm 1}$ is zero when $\beta_2 = \pi/2$, $\phi_2 = 0$. This shows that it is necessary to have knowledge of the other polarizations in the system in the τ_2 period. Equivalently it is necessary to know what the time development is for the full spin density matrix up to and including the final pulse. Thereafter only the single quantum modes are required in the final detection period.

Analysis of the triple pulse sequence Eq. [39] for $I = \frac{3}{2}$ along the lines of Section IV shows that the sequence $(\pi/2)_0\text{-}\tau_1\text{-}(\pi/2)_0\text{-}\tau_2$ produces ϕ^1_0, ϕ^3_0, $\phi^2_{\pm 2}$, and $\phi^3_{\pm 2}$, all other polarizations are zero. In this case, $\phi^2_{\pm 2}$ and $\phi^3_{\pm 2}$ do evolve under the quadrupole interaction (*8*). The third $(\pi/2)_0$ pulse produces a signal which includes echoes at $\tau_3 = \tau_1$, $\tau_2 - \tau_1$, τ_2 and $\tau_2 + \tau_1$. The primary echo at $\tau_3 = \tau_1$, contains information about dipolar and octupolar zero-quantum polarizations, whereas the three stimulated echoes contain information about the evolution of the quadrupolar and octupolar double quantum coherences during the period τ_2. Consequently, Fourier transformation of the stimulated echoes with respect to τ_2 produces the two lines of the double quantum spectrum.

The variety of experiments being performed in NMR today on solids, liquids, liquid crystal samples, etc., resulting in echoes, coherence transfer, 2-D spectroscopy, etc., in response to various pulse sequences all have in common the fact that they

manipulate the nuclear spin polarizations. As shown in this paper for the simple cases of $I = 1$ and $\frac{3}{2}$, the multipoles provide a convenient set of physically relevant quantities to describe the experiments.

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