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Visualization of Pulse Sequences in Frequency Space, with Application to INEPT and DEPT for AX Systems

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Visualization of pulse sequences by the vector model is inadequate when the frequency components contain contributions that do not transform as vectors. In this paper the vector model is abandoned and the INEPT and DEPT sequences are described in frequency, rather than time, space.

Visualization (*1*) of the spin dynamics throughout pulse sequences has usually relied on the vector model. In this model appeal is made to the rotation of magnetization vectors on the surface of a three-dimensional sphere, or projections of the sphere into two dimensions. Although such a description can rationalize some pulse sequences, it cannot easily be used to predict new results and it is only qualitative.

The main reason for the limitations of the vector model is that, except for an isolated spin of $\frac{1}{2}$, spin dynamics involves terms with higher than vector character. An accurate and predictive visualization must include such contributions.

In this paper a different procedure is suggested by which it is possible to faithfully predict the results of pulse sequences. The essential feature is to abandon the use of the time-domain transformations on a sphere and replace it with a frequency-domain treatment in which stick diagrams are used to represent frequency space (*2*). The procedure is illustrated with the well-known coherence transfer pulse sequences INEPT (*3–5*) and DEPT (*5,6*) on AX systems as seen in Fig. 1. Although any complete operator basis can be used to represent the spin density operator, in this work the multipole basis is chosen (*7*).

Description of pulse sequences usually focuses on the time evolution of various frequency components (*8*). In the time domain these simply oscillate according to

$$\exp(i\omega_0 t) \qquad [1]$$

whereas in the frequency domain, the oscillations become delta functions

$$\delta(\omega-\omega_0) \Rightarrow \underset{\omega_0}{\overline{\quad\vert\quad}}\qquad \omega \rightarrow. \qquad [2]$$

Before treating the INEPT and DEPT sequences, an example is given to show that Eq. [1] can contain more than vector character. Consider the simple case of a spin 1 with an axially symmetric quadrupole. The single-quantum coherences evolve from any initial condition according to (*9*)

$$\begin{bmatrix}\hat{\phi}^1_1(t)\\ \hat{\phi}^2_1(t)\end{bmatrix}=\begin{bmatrix}\cos\omega_Q t & \sin\omega_Q t\\ -\sin\omega_Q t & \cos\omega_Q t\end{bmatrix}\begin{bmatrix}\hat{\phi}^1_1(0)\\ \hat{\phi}^2_1(0)\end{bmatrix}, \qquad [3]$$

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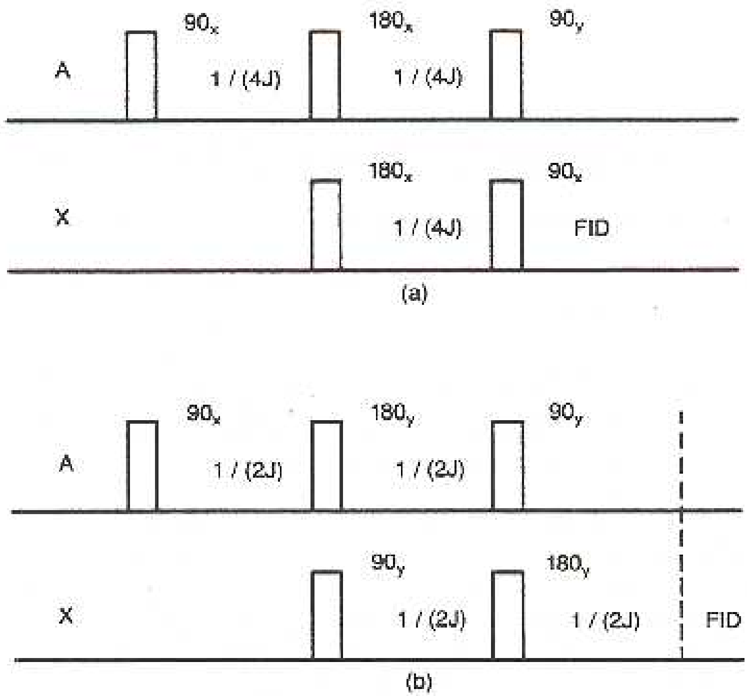


FIG. 1. (a) The INEPT sequence. (b) The DEPT sequence.

where ω_Q is the quadrupole constant. The polarizations are in the ω_0 rotating frame

$$\tilde{\phi}_q^k(t) = \exp(-iq\omega_0 t)\phi_q^k(t), \qquad [4]$$

where k is the multipole magnitude and q is the quantum number which is the order of the multiquantum coherence. The NMR experiment can measure only the vector $k = 1$ giving

$$\tilde{\phi}_1^1(t) = \cos \omega_Q t \tilde{\phi}_1^1(0) + \sin \omega_Q t \tilde{\phi}_1^2(0). \qquad [5]$$

The frequency components are given by

$$\exp(\pm i\omega_Q t) = [\tilde{\phi}_1^1(t) \mp i\tilde{\phi}_1^2(t)]/[\tilde{\phi}_1^1(0) \mp i\tilde{\phi}_1^2(0)]. \qquad [6]$$

This expression shows that each frequency has contributions from components which can transform like second-rank tensors. This nonvector character (sometimes accounted for as bilinear terms) should not be neglected for faithful descriptions of spin dynamics.

Figure 2 shows the Fourier transform of the single-quantum coherences $\tilde{\phi}_1^1(t)$ and $\tilde{\phi}_1^2(t)$. The intensities of the two components depend on how much $\tilde{\phi}_1^1(0)$ and $\tilde{\phi}_1^2(0)$ has been initially produced. Figure 3 and Eq. [6] show that each component $\exp(\pm i\omega_Q t)$ is a sum and difference of vector and quadrupolar single-quantum coherences. These results illustrate that when considering the evolution of one frequency component of the magnetization, it cannot be treated as a vector alone.

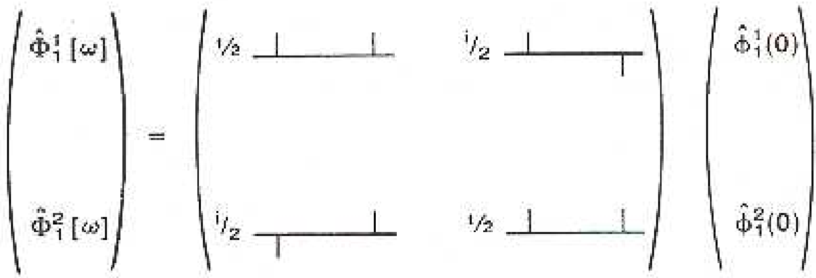


FIG. 2. Frequency contributions to single-quantum vector and second-rank tensor polarizations. Nonzero initial $\hat{\phi}_1^2(0)$ gives nonvector contributions to the observable $\hat{\Phi}_1^1[\omega]$.

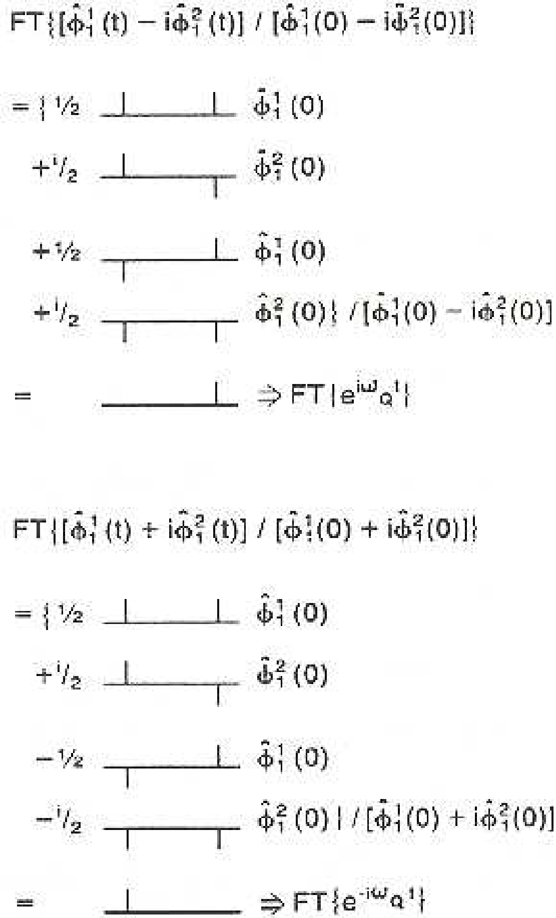


FIG. 3. The two lines of single-quantum coherence for a spin 1 (with symmetrical quadrupolar interaction) showing vector and nonvector decomposition.

Turning now to the INEPT and DEPT sequences, the usual rationale for the transfer of coherence between one spin and the other spin is to follow the development of phase differences between the faster and slower moving components after the initial 90° pulse on the first spin. The sequence is depicted in Fig. 4 and such an interpretation of the INEPT sequence is argued to enhance the population difference of the second spin.

An alternative rationale, which is quantitatively correct, represents the polarizations in matrix form. Table I gives the operator basis for two spins of $\frac{1}{2}$. Under the Hamiltonian

$$\mathscr{H}/h = (-\gamma_1 I_{1z} - \gamma_2 I_{2z})B_0 + J\mathbf{I}_1 \cdot \mathbf{I}_2 \qquad [7]$$

the set of coupled first-order differential equations for the single-quantum coherences is given by *(10)*, written here as

$$\dot{\Phi}_q(t) = i\mathcal{L}_q \cdot \Phi_q(t), \qquad [8]$$

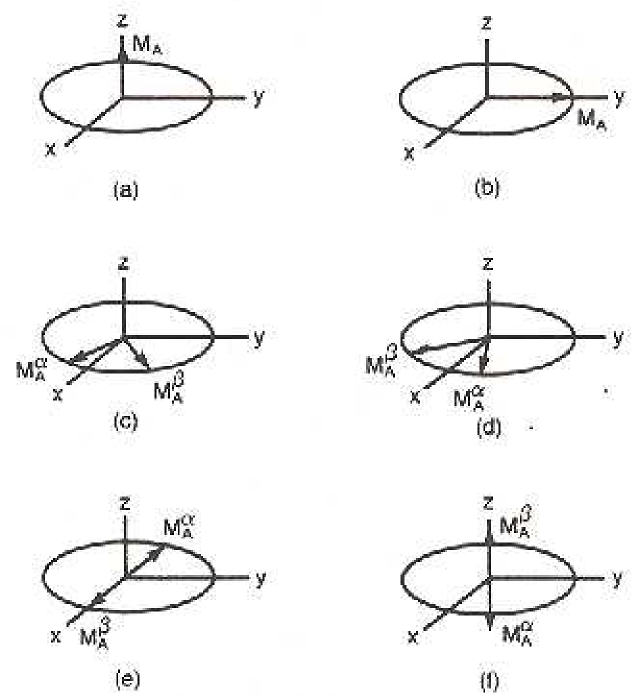


FIG. 4. The vector model visualization of the INEPT sequence for an AX system where the A spin magnetization vector is followed. (a) Initial magnetization M_A; (b) after an applied 90°_x(A) pulse; (c) dephasing of M_A for a period $\tau = 1/(4J)$; (d) after simultaneous 180° pulses, which has the effect of producing and interchanging the mirror images of the dephased M_A; (e) further dephasing for a period $\tau = 1/(4J)$; (f) after 90°_y(A) pulse in which magnetization is produced aligned about the z axis. The vector aligned along the $-z$ direction represents an inverted population.

TABLE 1

Two-Spin Multipole Operator Basis

Multipole operator	Spin operator	No. of components	Polarization
$T^{00}(00)$	Identity E	1	$\phi_0^0(00)$
$T^{00}(11)$	$\mathbf{I}_1 \cdot \mathbf{I}_2$	1	$\phi_0^0(11)$
$T^{1q}(10)$	$\mathbf{I}_1$	3	$\phi_q^1(10)$
$T^{1q}(01)$	$\mathbf{I}_2$	3	$\phi_q^1(01)$
$T^{1q}(11)$	$\mathbf{I}_1 \times \mathbf{I}_2$	3	$\phi_q^1(11)$
$T^{2q}(11)$	$[\mathbf{I}_1\mathbf{I}_2]^2$	5	$\phi_q^2(11)$

where the vector $\hat{\Phi}_q(t)$ has components $\hat{\phi}_q^k(k_1k_2)[t]$ and $\mathcal{L}_q$ is given by

$$\mathcal{L}_0 = \begin{bmatrix} 0 & \sqrt{8/3}\omega_D & 0 & 0 & 0 \\ \sqrt{8/3}\omega_D & 0 & 2/\sqrt{3}\omega_D & iJ/\sqrt{2} & -iJ/\sqrt{2} \\ 0 & 2/\sqrt{3}\omega_D & 0 & 0 & 0 \\ 0 & -iJ/\sqrt{2} & 0 & 0 & 0 \\ 0 & iJ/\sqrt{2} & 0 & 0 & 0 \end{bmatrix} \qquad [9]$$

and

$$\mathcal{L}_1 = \begin{bmatrix} \omega_D & 0 & -iJ/\sqrt{2} & 0 \\ 0 & -\omega_D & iJ/\sqrt{2} & 0 \\ iJ/\sqrt{2} & -iJ/\sqrt{2} & 0 & \omega_D \\ 0 & 0 & \omega_D & 0 \end{bmatrix}. \qquad [10]$$

Since this Hamiltonian does not mix coherences, the Liouville matrix blocks out in q so the 16×16 matrix becomes a 5×5 matrix for zero-quantum processes, two 4×4 matrices for single-quantum, and two 1×1 matrices for double-quantum, the last being simply

$$\phi_{\pm 2}^2(11)[t] = \exp[\pm i2\bar{\omega}t]\,\phi_{\pm 2}^2(11)[0], \qquad [11]$$

where

$$\bar{\omega} = 1/2(\omega_{01} + \omega_{02}), \qquad \omega_D = 1/2(\omega_{01} - \omega_{02}).$$

Solutions of these are straightforward giving

$$\hat{\Phi}_q(t) = \mathbf{M}^q(t)\,\hat{\Phi}_q(0), \qquad [12]$$

where $\hat{\Phi}_q(0)$ are the initial conditions. Initial conditions do not necessarily refer to the beginning of the pulse sequences, but rather to the set of polarizations produced immediately after any pulse in the sequence. Equation [12] is used to calculate the evolution of the spin system between pulses. The $\mathbf{M}^q$ matrices are given in paper XI (*10*), but specialized to an AX system, the $\mathbf{M}^q$ matrix for single-quantum coherences ($q = 1$) is given by the 4×4 matrix

$$\frac{1}{2}\begin{bmatrix} e^{i\lambda_1 t}+e^{i\lambda_2 t} & 0 & \frac{i}{\sqrt{2}}[e^{i\lambda_1 t}-e^{i\lambda_2 t}] & \frac{i}{\sqrt{2}}[e^{i\lambda_1 t}-e^{i\lambda_2 t}] \\ 0 & e^{-i\lambda_1 t}+e^{-i\lambda_2 t} & \frac{i}{\sqrt{2}}[e^{-i\lambda_1 t}-e^{-i\lambda_2 t}] & \frac{-i}{\sqrt{2}}[e^{-i\lambda_1 t}-e^{-i\lambda_2 t}] \\ \frac{-i}{\sqrt{2}}[e^{i\lambda_1 t}-e^{i\lambda_2 t}] & \frac{-i}{\sqrt{2}}[e^{-i\lambda_1 t}-e^{-i\lambda_2 t}] & \cos\lambda_1 t+\cos\lambda_2 t & i[\sin\lambda_1 t+\sin\lambda_2 t] \\ \frac{-i}{\sqrt{2}}[e^{i\lambda_1 t}-e^{i\lambda_2 t}] & \frac{-i}{\sqrt{2}}[e^{-i\lambda_1 t}-e^{-i\lambda_2 t}] & i[\sin\lambda_1 t+\sin\lambda_2 t] & \cos\lambda_1 t+\cos\lambda_2 t \end{bmatrix}, \quad [13]$$

where the four frequencies are

$$\lambda_{\pm 2} \simeq \pm\Delta\omega \pm J/2, \qquad \lambda_{\pm 1} \simeq \pm\Delta\omega \mp J/2 \qquad \Delta\omega = \omega_{01} - \omega_{02} \quad [14]$$

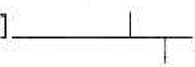
while the vector $\hat{\Phi}_1(t)$ is composed of the set of single-quantum coherences

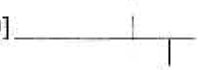
$$\hat{\Phi}_1(t) = \{\hat{\phi}_1^1(10)[t], \hat{\phi}_1^1(01)[t], \hat{\phi}_1^1(11)[t], \hat{\phi}_1^2(11)[t]\}. \quad [15]$$

Equation [12] gives the evolution of the single-quantum coherences from all initial conditions $\hat{\phi}_1^k(k_1k_2)[0]$.

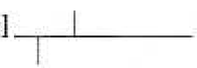
An easier way of viewing possible processes is to Fourier transform Eq. [13] and replace the oscillations with delta functions. This gives an equation shown in Fig. 5.

From Fig. 5 the observable, spin number 1, obeys

$\hat{\Phi}_1^1(10)[\omega] = 1/2\{\hat{\phi}_1^1(10)[0]$  $+\, i/\sqrt{2}\hat{\phi}_1^1(11)[0]$ 

$+\, i/\sqrt{2}\hat{\phi}_1^2(11)[0]$  $\}$ [16]

while for spin 2

$\hat{\Phi}_1^1(01)[\omega] = 1/2\{\hat{\phi}_1^1(01)[0]$  $+\, i/\sqrt{2}\hat{\phi}_1^1(11)[0]$ 

$+\, i/\sqrt{2}\hat{\phi}_1^2(11)[0]$  $\}$ [17]

within the AX approximation, no further single-quantum coherences exist.

The Zeeman-field aligned polarizations of the two spins $\hat{\phi}_0^1(10)$ and $\hat{\phi}_0^1(01)$ are the only initial nonzero quantities. These populations are dependent on the gyromagnetic

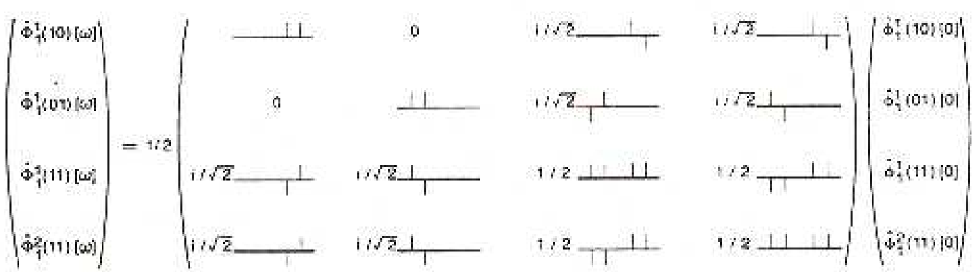


FIG. 5. Fourier transform of the time evolution matrix for single-quantum coherences in AX approximation with the sticks denoting frequencies.

ratios of spin 1 and spin 2, respectively. By cycling the phases of the pulses applied to the "insensitive" nuclei, contributions to the signal from $\tilde{\phi}_0^1(01)$ can be subtracted. To determine the polarization transfer pathway of $\tilde{\phi}_0^1(10)$, we can consider only $\tilde{\phi}_0^1(10) \neq 0$ initially. The INEPT sequence converts this initial nonzero $\tilde{\phi}_0^1(10)[0]$ to $\tilde{\phi}_{\pm1}^1(11) = -\tilde{\phi}_{\pm1}^2(11)$ at the end of the sequence. Likewise, the DEPT sequence converts the initial nonzero $\tilde{\phi}_0^1(10)[0]$ to $\tilde{\phi}_{\pm1}^1(11) = -\tilde{\phi}_{\pm1}^2(11)$ immediately after the third set of pulses. By waiting for a period $\tau = 1/(2J)$, however, before collecting the FID, these single-quantum bilinear polarizations reevolve into nonzero $\tilde{\phi}_{\pm1}^1(01)$. As can be seen from Eq. [16], these products result in the familiar frequency spectra for an AX system, which in the case of INEPT is a doublet in which the two lines are 180° out of phase and in the case of DEPT is a normal undistorted doublet.

The above treatment is predictive in the sense that it quantitatively gives a way of planning pulse sequences. It is clear by inspection of the frequency matrix (Fig. 5) what conditions must be fulfilled for coherence transfer. It does not give clues as to what pathway must be followed to convert the spin polarizations to the desired form. It is important to note that the pathway from initial to final polarizations in the INEPT sequence involves only single-quantum coherences. Hence, the observed signal enhancement is a result of coherence transfer rather than population transfer. This distinction is less evident in the DEPT sequence as its pathway involves polarizations other than single-quantum ones. These results are a consequence of simultaneous pulses on the two spins. Nonsimultaneous pulses will introduce other multiquantum coherences.

It is possible to follow the polarizations throughout the pulse sequence by more detailed calculation. As an example, Table 2 gives the nonzero polarizations which are produced at each stage of INEPT. In the INEPT sequence, the single-quantum polarizations prior to the final analyzing pulse have as a dependence on the evolution period τ_1 terms involving $\cos(2\pi(\lambda_2 - \lambda_1)\tau_1)$ and $\sin(2\pi(\lambda_2 - \lambda_1)\tau_1)$. For INEPT, the argument is chosen to be

$$2\pi(\lambda_2 - \lambda_1)\tau_1 = \pi/2. \qquad [18]$$

This requires $\tau_1 = 1/(4J)$ as expected, the difference in eigenvalues being

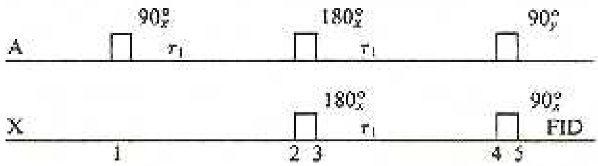
$$\lambda_2 - \lambda_1 = J. \qquad [19]$$

What this effectively does is maximize coherence transfer to the bilinear single-quantum polarizations $\tilde{\phi}_{\pm1}^1(11)$ and $\tilde{\phi}_{\pm1}^2(11)$. Hence, polarization transfer between spins occurs in the INEPT sequence through the single-quantum bilinear terms.

In the DEPT sequence, the dependence of the single-quantum polarizations on the evolution period τ_1 is much more complex due to the mixing of polarizations other than the single-quantum ones. The choice of $\tau_1 = 1/(2J)$ is made to maximize coherence transfer to the single-quantum bilinear polarizations $\tilde{\phi}_{\pm1}^1(11)$ and $\tilde{\phi}_{\pm1}^2(11)$, as in the INEPT sequence.

For completeness it is useful to note which other polarizations are nonzero after the INEPT and DEPT sequences. From Table 2, there are zero-quantum bilinear terms which all oscillate in phase during the acquisition period along the z axis:

TABLE 2
The Nonzero Polarizations at Steps throughout the INEPT Sequence



Stage	Nonzero polarizations	Expression (to a phase)
1	$\hat{\phi}^1_{\pm 1}(10)$	$1/\sqrt{2}$
2	$\hat{\phi}^1_{\pm 1}(10)$	$1/(2\sqrt{2})[e^{\pm i\lambda_1\tau_1} + e^{\pm i\lambda_2\tau_1}]$
	$\hat{\phi}^1_{\pm 1}(11)$	$i/4[\mp e^{\pm i\lambda_1\tau_1} \pm e^{\pm i\lambda_2\tau_1}]$
	$\hat{\phi}^2_{\pm 1}(11)$	$i/4[-e^{\pm i\lambda_1\tau_1} + e^{\pm i\lambda_2\tau_1}]$
3	$\hat{\phi}^1_{\pm 1}(10)$	$1/(2\sqrt{2})[-e^{\mp i\lambda_1\tau_1} - e^{\mp i\lambda_2\tau_1}]$
	$\hat{\phi}^1_{\pm 1}(11)$	$i/4[\mp e^{\mp i\lambda_1\tau_1} \pm e^{\mp i\lambda_2\tau_1}]$
	$\hat{\phi}^2_{\pm 1}(11)$	$i/4[-e^{\mp i\lambda_1\tau_1} + e^{\mp i\lambda_2\tau_1}]$
4	$\hat{\phi}^1_{\pm 1}(10)$	$-1/\sqrt{2}\cos(\lambda_2 - \lambda_1)\tau_1$
	$\hat{\phi}^1_{\pm 1}(11)$	$1/2\sin(\lambda_2 - \lambda_1)\tau_1$
	$\hat{\phi}^2_{\pm 1}(11)$	$1/2\sin(\lambda_2 - \lambda_1)\tau_1$
5	$\hat{\phi}^1_0(10)$	$-1/2\cos(\lambda_2 - \lambda_1)\tau_1$
	$\hat{\phi}^1_{\pm 1}(10)$	$-1/(2\sqrt{2})\cos(\lambda_2 - \lambda_1)\tau_1$
	$\hat{\phi}^0_0(11)$	$i/(4\sqrt{3})\sin(\lambda_2 - \lambda_1)\tau_1$
	$\hat{\phi}^1_0(11)$	$i/(4\sqrt{2})\sin(\lambda_2 - \lambda_1)\tau_1$
	$\hat{\phi}^2_0(11)$	$i/(4\sqrt{6})\sin(\lambda_2 - \lambda_1)\tau_1$
	$\hat{\phi}^1_{\pm 1}(11)$	$\pm i/4\sin(\lambda_2 - \lambda_1)\tau_1$
	$\hat{\phi}^2_{\pm 1}(11)$	$-i/4\sin(\lambda_2 - \lambda_1)\tau_1$
	$\hat{\phi}^2_{\pm 2}(11)$	$i/4\sin(\lambda_2 - \lambda_1)\tau_1$

$$\hat{\phi}^1_0(11)[t] = \sqrt{2/3}\,\hat{\phi}^0_0(11)[t] \quad [20]$$

$$\hat{\phi}^2_0(11)[t] = \sqrt{2}\,\hat{\phi}^0_0(11)[t] \quad [21]$$

$$\hat{\phi}^0_0(11)[t] \neq 0. \quad [22]$$

Equally interesting is that the z magnetizations associated with spin 1 and spin 2 in the acquisition period are identically zero:

$$\hat{\phi}^1_0(10) = 0 \quad [23]$$

$$\hat{\phi}^1_0(01) = 0. \quad [24]$$

This along with the other zero-quantum coherences means that the populations of the four levels are all equal;

$$P_{\alpha\alpha} = P_{\alpha\beta} = P_{\beta\alpha} = P_{\beta\beta} \quad [25]$$

in the acquisition period of the INEPT and DEPT sequences.

The main feature of the approach described in this paper is the representation of the development of the multiquantum coherences as a matrix in frequency space. All the initial conditions are displayed and the possible processes are clearly evident. To summarize, from Fig. 2 the INEPT sequence requires a change in polarizations of

$$\begin{bmatrix} \hat{\phi}^{1}_{\pm 1}(10) \\ 0 \\ 0 \\ 0 \end{bmatrix} \rightarrow \begin{bmatrix} 0 \\ 0 \\ \hat{\phi}^{1}_{\pm 1}(11) \\ \hat{\phi}^{2}_{\pm 1}(11) \end{bmatrix} = -\hat{\phi}^{1}_{\pm 1}(11) \qquad \text{INEPT} \qquad [26]$$

while the DEPT sequence entails

$$\begin{bmatrix} \hat{\phi}^{1}_{\pm 1}(10) \\ 0 \\ 0 \\ 0 \end{bmatrix} \rightarrow \begin{bmatrix} 0 \\ \hat{\phi}^{1}_{\pm 1}(01) \\ 0 \\ 0 \end{bmatrix} \qquad \text{DEPT.} \qquad [27]$$

Variations on this basic idea will permit faithful representations of 2-D experiments, such as the COSY, etc. Extensions to higher multispin systems are possible and the ease of doing this depends on the ease of obtaining the development matrix $\mathbf{M}^{\mathrm{v}}$. Although the actual means of how the polarizations are transferred is not obtained by this or other methods, having the initial and final requirements for all possible processes should aid in the construction of basic pulse sequences. Also, this method defines a pathway through which spins can exchange polarizations, namely through the bilinear polarizations (or multilinear polarizations if considering higher multispin systems).

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