

# Analytical Polarization and Coherence Transfer Functions for Three Dipolar Coupled Spins $\frac{1}{2}$

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**Analytical polarization and coherence transfer functions are presented for a spin system consisting of three dipolar coupled homonuclear spins  $\frac{1}{2}$  under energy matched conditions. Based on these transfer functions, optimal durations of Hartmann–Hahn mixing periods can be determined for arbitrary dipolar coupling constants  $D_{12}$ ,  $D_{13}$ , and  $D_{23}$ . In addition, the dependence of the transfer efficiency on the relative size of the dipolar coupling constants is illustrated.** © 2000 Academic Press

**Key Words:** Hartmann–Hahn transfer; dipolar coupling; analytical transfer functions; DCOSY.

$$\mathcal{H}_D = 2\pi \sum_{i < j}^3 D_{ij} \{2I_{iz}I_{jz} - I_{ix}I_{jx} - I_{iy}I_{jy}\}. \quad [1]$$

Here the  $z$  axis is the quantization axis. In analogy to the case of three coupled spins under planar mixing conditions (17), polarization transfer functions can be derived based on the eigenvalues and eigenfunctions of  $\mathcal{H}_D$ . The product

## INTRODUCTION

Hartmann–Hahn transfer based on effective isotropic or planar coupling tensors is commonly used in high-resolution NMR (1–3). For a number of simple spin systems, analytical solutions are known for coherence and polarization transfer functions in isotropic (4–9) or planar mixing experiments (5, 10–17). Recently, Hansen *et al.* (18) introduced the DCOSY experiment (dipolar coupling spectroscopy), which is based on homonuclear Hartmann–Hahn transfer through residual dipolar couplings (19, 20) in high-resolution NMR. This experiment makes it possible to transfer magnetization between spins that are separated by even more than 7 Å. Transfer functions of transverse and longitudinal magnetization are well known for the simple two-spin system (3, 18). However, for more than two dipolar coupled spins, transfer functions are considerably more complicated and could so far only be calculated using numerical simulations (21). Here we present analytical transfer functions for the general case of three dipolar coupled spins with arbitrary effective coupling constants.

## THEORY

We consider a system consisting of three homonuclear spins  $\frac{1}{2}$  with (effective) dipolar coupling constants  $D_{ij}$ . If the effective fields are zero, the Hamiltonian has the form

**TABLE 1**  
General Transfer Functions  $T_{A \rightarrow B}$  for  $A = I_z$

$$\begin{aligned} T_{I_{1z} \rightarrow I_{1z}} &= T_{11}^z = 1 - \sum_{i=1}^3 \sum_{j=i+1}^3 \frac{1}{2} w_{ij}^2 \{1 - \cos(\Delta_{ij}\tau)\} \\ T_{I_{1z} \rightarrow I_{2z}} &= T_{12}^z = \sum_{i=1}^3 \sum_{j=i+1}^3 \frac{1}{2} \{(\gamma_i\gamma_j - \beta_i\beta_j)^2 - (\alpha_i\alpha_j)^2\} \{1 - \cos(\Delta_{ij}\tau)\} \\ T_{I_{1z} \rightarrow I_{3z}} &= T_{13}^z = \sum_{i=1}^3 \sum_{j=i+1}^3 \frac{1}{2} \{(\alpha_i\alpha_j - \gamma_i\gamma_j)^2 - (\beta_i\beta_j)^2\} \{1 - \cos(\Delta_{ij}\tau)\} \\ T_{I_{1z} \rightarrow \{I_{1z}I_{2y} - I_{2z}I_{1y}\}} &= \sum_{i=1}^3 \sum_{j=i+1}^3 \frac{1}{2} \{(\beta_i\gamma_j - \gamma_i\beta_j)w_{ij}\} \sin(\Delta_{ij}\tau) \\ T_{I_{1z} \rightarrow \{I_{1z}I_{3y} - I_{3z}I_{1y}\}} &= \sum_{i=1}^3 \sum_{j=i+1}^3 \frac{1}{2} \{(\alpha_i\gamma_j - \gamma_i\alpha_j)w_{ij}\} \sin(\Delta_{ij}\tau) \\ T_{I_{1z} \rightarrow \{I_{2z}I_{3y} - I_{3z}I_{2y}\}} &= \sum_{i=1}^3 \sum_{j=i+1}^3 \frac{1}{2} \{(\alpha_i\beta_j - \beta_i\alpha_j)w_{ij}\} \sin(\Delta_{ij}\tau) \\ T_{I_{1z} \rightarrow \{I_{1z}(I_{2z}I_{3x} + I_{2y}I_{3y})\}} &= \sum_{i=1}^3 \sum_{j=i+1}^3 \frac{1}{4} \{(\beta_i\alpha_j + \alpha_i\beta_j)w_{ij}\} \{1 - \cos(\Delta_{ij}\tau)\} \\ T_{I_{1z} \rightarrow \{I_{2z}(I_{1z}I_{3x} + I_{1y}I_{3y})\}} &= \sum_{i=1}^3 \sum_{j=i+1}^3 \frac{1}{4} \{(\alpha_i\gamma_j + \gamma_i\alpha_j)w_{ij}\} \{1 - \cos(\Delta_{ij}\tau)\} \\ T_{I_{1z} \rightarrow \{I_{3z}(I_{1z}I_{2x} + I_{1y}I_{2y})\}} &= \sum_{i=1}^3 \sum_{j=i+1}^3 \frac{1}{4} \{(\gamma_i\beta_j + \beta_i\gamma_j)w_{ij}\} \{1 - \cos(\Delta_{ij}\tau)\} \end{aligned}$$

Note.  $\alpha_i$ ,  $\beta_i$ ,  $\gamma_i$  are defined in Eqs. [7]–[10], and  $w_{ij} = -\alpha_i\alpha_j - \beta_i\beta_j + \gamma_i\gamma_j$ .

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**TABLE 2**  
**General Transfer Functions  $T_{A \rightarrow B}$  for  $A = I_{1x}$**

$$\begin{aligned}
T_{I_{1x} \rightarrow I_{1x}} &= T_{11}^x = \sum_{i=1}^3 \alpha_i^2 \beta_i^2 + \frac{1}{2} \sum_{i=1}^3 \gamma_i^2 \cos(\Delta_{0i}\tau) + \frac{1}{2} \sum_{i=1}^3 \sum_{j=i+1}^3 \nu_{ij}^2 \cos(\Delta_{ij}\tau) \\
T_{I_{1x} \rightarrow I_{2x}} &= T_{12}^x = \sum_{i=1}^3 \alpha_i^2 \beta_i \gamma_i + \frac{1}{2} \sum_{i=1}^3 \beta_i \gamma_i \cos(\Delta_{0i}\tau) + \frac{1}{2} \sum_{i=1}^3 \sum_{j=i+1}^3 \nu_{ij} (\alpha_i \gamma_j + \alpha_j \gamma_i) \cos(\Delta_{ij}\tau) \\
T_{I_{1x} \rightarrow I_{3x}} &= T_{13}^x = \sum_{i=1}^3 \alpha_i \beta_i^2 \gamma_i + \frac{1}{2} \sum_{i=1}^3 \alpha_i \gamma_i \cos(\Delta_{0i}\tau) + \frac{1}{2} \sum_{i=1}^3 \sum_{j=i+1}^3 \nu_{ij} (\beta_i \gamma_j + \beta_j \gamma_i) \cos(\Delta_{ij}\tau) \\
T_{I_{1x} \rightarrow I_{12}I_{2y}} &= \sum_{i=1}^3 \beta_i \gamma_i \sin(\Delta_{0i}\tau) + \sum_{i=1}^3 \sum_{j=i+1}^3 \nu_{ij} (\alpha_i \gamma_j - \alpha_j \gamma_i) \sin(\Delta_{ij}\tau) \\
T_{I_{1x} \rightarrow I_{22}I_{1y}} &= \sum_{i=1}^3 \gamma_i^2 \sin(\Delta_{0i}\tau) + \sum_{i=1}^3 \sum_{j=i+1}^3 \nu_{ij} (\alpha_i \beta_j - \alpha_j \beta_i) \sin(\Delta_{ij}\tau) \\
T_{I_{1x} \rightarrow I_{12}I_{3y}} &= \sum_{i=1}^3 \alpha_i \gamma_i \sin(\Delta_{0i}\tau) + \sum_{i=1}^3 \sum_{j=i+1}^3 \nu_{ij} (\beta_i \gamma_j - \beta_j \gamma_i) \sin(\Delta_{ij}\tau) \\
T_{I_{1x} \rightarrow I_{32}I_{1y}} &= \sum_{i=1}^3 \gamma_i^2 \sin(\Delta_{0i}\tau) - \sum_{i=1}^3 \sum_{j=i+1}^3 \nu_{ij} (\alpha_i \beta_j - \alpha_j \beta_i) \sin(\Delta_{ij}\tau) \\
T_{I_{1x} \rightarrow I_{22}I_{3y}} &= \sum_{i=1}^3 \alpha_i \gamma_i \sin(\Delta_{0i}\tau) - \sum_{i=1}^3 \sum_{j=i+1}^3 \nu_{ij} (\beta_i \gamma_j - \beta_j \gamma_i) \sin(\Delta_{ij}\tau) \\
T_{I_{1x} \rightarrow I_{32}I_{2y}} &= \sum_{i=1}^3 \beta_i \gamma_i \sin(\Delta_{0i}\tau) - \sum_{i=1}^3 \sum_{j=i+1}^3 \nu_{ij} (\alpha_i \gamma_j - \alpha_j \gamma_i) \sin(\Delta_{ij}\tau) \\
T_{I_{1x} \rightarrow I_{12}I_{2y}I_{3y}} &= 2 \sum_{i=1}^3 \alpha_i \beta_i (\alpha_i^2 + \beta_i^2 - \gamma_i^2) + 2 \sum_{i=1}^3 \sum_{j=i+1}^3 \nu_{ij} (\alpha_i \alpha_j + \beta_i \beta_j - \gamma_i \gamma_j) \cos(\Delta_{ij}\tau) \\
T_{I_{1x} \rightarrow I_{22}I_{1y}I_{3y}} &= 2 \sum_{i=1}^3 \alpha_i \beta_i (\alpha_i^2 - \beta_i^2 + \gamma_i^2) + 2 \sum_{i=1}^3 \sum_{j=i+1}^3 \nu_{ij} (\alpha_i \alpha_j - \beta_i \beta_j + \gamma_i \gamma_j) \cos(\Delta_{ij}\tau) \\
T_{I_{1x} \rightarrow I_{32}I_{1y}I_{2y}} &= 2 \sum_{i=1}^3 \alpha_i \beta_i (-\alpha_i^2 + \beta_i^2 + \gamma_i^2) + 2 \sum_{i=1}^3 \sum_{j=i+1}^3 \nu_{ij} (-\alpha_i \alpha_j + \beta_i \beta_j + \gamma_i \gamma_j) \cos(\Delta_{ij}\tau) \\
T_{I_{1x} \rightarrow I_{12}I_{2y}I_{3z}} &= -4 \sum_{i=1}^3 \alpha_i^2 \beta_i^2 + 2 \sum_{i=1}^3 \gamma_i^2 \cos(\Delta_{0i}\tau) - 2 \sum_{i=1}^3 \sum_{j=i+1}^3 \nu_{ij}^2 \cos(\Delta_{ij}\tau) \\
T_{I_{1x} \rightarrow I_{22}I_{1y}I_{3z}} &= -4 \sum_{i=1}^3 \alpha_i^2 \beta_i \gamma_i + 2 \sum_{i=1}^3 \beta_i \gamma_i \cos(\Delta_{0i}\tau) - 2 \sum_{i=1}^3 \sum_{j=i+1}^3 \nu_{ij} (\alpha_i \gamma_j + \alpha_j \gamma_i) \cos(\Delta_{ij}\tau) \\
T_{I_{1x} \rightarrow I_{32}I_{1y}I_{2z}} &= -4 \sum_{i=1}^3 \alpha_i \beta_i^2 \gamma_i + 2 \sum_{i=1}^3 \alpha_i \gamma_i \cos(\Delta_{0i}\tau) - 2 \sum_{i=1}^3 \sum_{j=i+1}^3 \nu_{ij} (\beta_i \gamma_j + \beta_j \gamma_i) \cos(\Delta_{ij}\tau)
\end{aligned}$$

Note.  $\alpha_i$ ,  $\beta_i$ ,  $\gamma_i$  are defined in Eqs. [7]–[10], and  $\nu_{ij} = (\alpha_i \beta_j + \alpha_j \beta_i)$ .

functions  $|\alpha\alpha\alpha\rangle$  (with magnetic quantum number  $m = \frac{3}{2}$ ),  $|\beta\alpha\alpha\rangle$ ,  $|\alpha\beta\alpha\rangle$ ,  $|\alpha\alpha\beta\rangle$  (with  $m = \frac{1}{2}$ ),  $|\alpha\beta\beta\rangle$ ,  $|\beta\alpha\beta\rangle$ ,  $|\beta\beta\alpha\rangle$  (with  $m = -\frac{1}{2}$ ), and  $|\beta\beta\beta\rangle$  (with  $m = -\frac{3}{2}$ ) form a convenient set of basis functions. In this basis the matrix representation of  $\mathcal{H}_D$  assumes a simple block structure because  $\mathcal{H}_D$  commutes with  $F_z = I_{1z} + I_{2z} + I_{3z}$ . Nonzero matrix elements exist only between basis functions with identical

magnetic quantum numbers  $m$ . For  $m = \frac{3}{2}$  and  $m = -\frac{3}{2}$ , the resulting blocks are identical  $1 \times 1$  matrices:

$$\mathcal{H}_D^{(3/2)} = \mathcal{H}_D^{(-3/2)} = \pi(D_{12} + D_{13} + D_{23}) = \lambda_0. \quad [2]$$

For  $m = \frac{1}{2}$  and  $m = -\frac{1}{2}$ , the blocks are identical  $3 \times 3$  matrices

**TABLE 3**  
**Simplified Transfer Functions  $T_{kl}^x = T_{I_{k\alpha} \rightarrow I_{l\alpha}}$  for Special Case 1**  
**( $D_{12} = D_{13} = D_{23}/2 = D$ ) with  $\alpha = z$  or  $x$**

$$\begin{aligned}
T_{11}^z &= \frac{5}{6} + \frac{1}{6} \cos(2\sqrt{6}\pi D\tau) \\
T_{12}^z &= T_{13}^z = \frac{1}{12} - \frac{1}{12} \cos(2\sqrt{6}\pi D\tau) \\
T_{22}^z &= T_{33}^z = \frac{11}{24} + \frac{1}{24} \cos(2\sqrt{6}\pi D\tau) + \frac{3 + \sqrt{6}}{12} \cos((2 + \sqrt{6})\pi D\tau) \\
&\quad + \frac{3 - \sqrt{6}}{12} \cos((2 - \sqrt{6})\pi D\tau) \\
T_{23}^z &= \frac{11}{24} + \frac{1}{24} \cos(2\sqrt{6}\pi D\tau) - \frac{3 + \sqrt{6}}{12} \cos((2 + \sqrt{6})\pi D\tau) \\
&\quad - \frac{3 - \sqrt{6}}{12} \cos((2 - \sqrt{6})\pi D\tau) \\
T_{11}^x &= \frac{11}{24} + \frac{1}{24} \cos(2\sqrt{6}\pi D\tau) + \frac{3 - \sqrt{6}}{12} \cos((6 + \sqrt{6})\pi D\tau) \\
&\quad + \frac{3 + \sqrt{6}}{12} \cos((6 - \sqrt{6})\pi D\tau) \\
T_{12}^x &= T_{13}^x = \frac{1}{12} - \frac{1}{12} \cos(2\sqrt{6}\pi D\tau) + \frac{1}{4\sqrt{6}} \cos((6 + \sqrt{6})\pi D\tau) \\
&\quad - \frac{1}{4\sqrt{6}} \cos((6 - \sqrt{6})\pi D\tau) \\
T_{22}^x &= T_{33}^x = \frac{1}{12} + \frac{1}{6} \cos(2\sqrt{6}\pi D\tau) + \frac{1}{4} \cos(4\pi D\tau) \\
&\quad + \left(\frac{1}{8} + \frac{1}{4\sqrt{6}}\right) \cos((6 + \sqrt{6})\pi D\tau) \\
&\quad + \left(\frac{1}{8} - \frac{1}{4\sqrt{6}}\right) \cos((6 - \sqrt{6})\pi D\tau) \\
&\quad + \left(\frac{1}{8} - \frac{1}{4\sqrt{6}}\right) \cos((2 + \sqrt{6})\pi D\tau) \\
&\quad + \left(\frac{1}{8} + \frac{1}{4\sqrt{6}}\right) \cos((2 - \sqrt{6})\pi D\tau) \\
T_{23}^x &= \frac{1}{12} + \frac{1}{6} \cos(2\sqrt{6}\pi D\tau) - \frac{1}{4} \cos(4\pi D\tau) \\
&\quad + \frac{3 + \sqrt{6}}{24} \cos((6 + \sqrt{6})\pi D\tau) + \frac{3 - \sqrt{6}}{24} \cos((6 - \sqrt{6})\pi D\tau) \\
&\quad - \frac{3 - \sqrt{6}}{24} \cos((2 + \sqrt{6})\pi D\tau) - \frac{3 + \sqrt{6}}{24} \cos((2 - \sqrt{6})\pi D\tau)
\end{aligned}$$

$$\mathcal{H}_D^{(1/2)} = \mathcal{H}_D^{(-1/2)} = -\pi \begin{pmatrix} S_1 & D_{12} & D_{13} \\ D_{12} & S_2 & D_{23} \\ D_{13} & D_{23} & S_3 \end{pmatrix}, \quad [3]$$

with

$$S_i = D_{ij} + D_{ik} - D_{jk} \quad [4]$$

for  $\{ijk\} = \{123\}, \{231\}$  and  $\{312\}$  and  $D_{ij} = D_{ji}$ .

The eigenvalues of the  $3 \times 3$  matrix of Eq. [3] are given by

$$\lambda_1 = 0$$

$$\lambda_{2,3} = -\frac{\lambda_0}{2} \mp \frac{\pi W}{2}, \quad [5]$$

with

$$W^2 = \sum_{i < j}^3 9D_{ij}^2 - \sum_{i=1}^3 6D_{ij}D_{ik}, \quad [6]$$

where in the second summation  $\{ijk\} = \{123\}, \{231\}$ , and  $\{312\}$ .

For each of the eigenvalues  $\lambda_i$  ( $i = 1, 2$ , or  $3$ ), the corresponding normalized eigenvectors are given by  $(\alpha_i, \beta_i, \gamma_i) = (\alpha'_i, \beta'_i, \gamma'_i)/n_i$  with the normalization constants

$$n_i = \sqrt{(\alpha'_i)^2 + (\beta'_i)^2 + (\gamma'_i)^2} \quad [7]$$

**TABLE 4**  
**Simplified Transfer Functions  $T_{kl}^x = T_{I_{k\alpha} \rightarrow I_{l\alpha}}$  for Special Case 2**  
**( $D_{12} = D_{13} = D$  and  $D_{23} = 0$ ) with  $\alpha = z$  or  $x$**

$$\begin{aligned}
T_{11}^z &= \frac{4}{6} + \frac{2}{6} \cos(2\sqrt{3}\pi D\tau) \\
T_{12}^z &= T_{13}^z = \frac{1}{6} - \frac{1}{6} \cos(2\sqrt{3}\pi D\tau) \\
T_{22}^z &= T_{33}^z = \frac{5}{12} + \frac{1}{12} \cos(2\sqrt{3}\pi D\tau) + \frac{3 - \sqrt{3}}{12} \cos((1 + \sqrt{3})\pi D\tau) \\
&\quad + \frac{3 + \sqrt{3}}{12} \cos((1 - \sqrt{3})\pi D\tau) \\
T_{23}^z &= \frac{5}{12} + \frac{1}{12} \cos(2\sqrt{3}\pi D\tau) - \frac{3 - \sqrt{3}}{12} \cos((1 + \sqrt{3})\pi D\tau) \\
&\quad - \frac{3 + \sqrt{3}}{12} \cos((1 - \sqrt{3})\pi D\tau) \\
T_{11}^x &= \frac{5}{12} + \frac{1}{12} \cos(2\sqrt{3}\pi D\tau) + \frac{3 + \sqrt{3}}{12} \cos((3 + \sqrt{3})\pi D\tau) \\
&\quad + \frac{3 - \sqrt{3}}{12} \cos((3 - \sqrt{3})\pi D\tau) \\
T_{12}^x &= T_{13}^x = -\frac{1}{12} + \frac{1}{12} \cos(2\sqrt{3}\pi D\tau) + \frac{1}{2\sqrt{3}} \cos((3 + \sqrt{3})\pi D\tau) \\
&\quad - \frac{1}{2\sqrt{3}} \cos((3 - \sqrt{3})\pi D\tau) \\
T_{22}^x &= T_{33}^x = \frac{1}{6} + \frac{1}{12} \cos(2\sqrt{3}\pi D\tau) + \frac{1}{4} \cos(2\pi D\tau) \\
&\quad + \frac{3 - \sqrt{3}}{24} \cos((3 + \sqrt{3})\pi D\tau) + \left(\frac{1}{8} + \frac{1}{4\sqrt{3}}\right) \cos((3 - \sqrt{3})\pi D\tau) \\
&\quad + \left(\frac{1}{8} + \frac{1}{4\sqrt{3}}\right) \cos((1 + \sqrt{3})\pi D\tau) + \left(\frac{1}{8} - \frac{1}{4\sqrt{3}}\right) \cos((1 - \sqrt{3})\pi D\tau) \\
T_{23}^x &= \frac{1}{6} + \frac{1}{12} \cos(2\sqrt{3}\pi D\tau) - \frac{1}{4} \cos(2\pi D\tau) \\
&\quad + \frac{3 - \sqrt{3}}{24} \cos((3 + \sqrt{3})\pi D\tau) + \frac{3 + \sqrt{3}}{24} \cos((3 - \sqrt{3})\pi D\tau) \\
&\quad - \frac{3 + \sqrt{3}}{24} \cos((1 + \sqrt{3})\pi D\tau) - \frac{3 - \sqrt{3}}{24} \cos((1 - \sqrt{3})\pi D\tau)
\end{aligned}$$

and

$$\alpha'_1 = D_{13} - D_{23}$$

$$\alpha'_{2,3} = -3(D_{12} - D_{23})^2 - 2D_{12}D_{23} + D_{12}D_{13} + D_{13}D_{23} \pm (D_{12} - D_{23})W \quad [8]$$

$$\beta'_1 = D_{23} - D_{12}$$

$$\beta'_{2,3} = -3(D_{13} - D_{23})^2 - 2D_{13}D_{23} + D_{12}D_{13} + D_{12}D_{23} \pm (D_{13} - D_{23})W \quad [9]$$

$$\gamma'_1 = D_{12} - D_{13}$$

$$\gamma'_{2,3} = 4D_{12}D_{13} - 2D_{12}D_{23} - 2D_{13}D_{23}. \quad [10]$$

Equations [8]–[10] represent the eigenvector components in all cases where the eigenvalues (Eq. [5]) are nondegenerate, i.e., if  $\lambda_1 \neq \lambda_2$ ,  $\lambda_1 \neq \lambda_3$ , and  $\lambda_2 \neq \lambda_3$ . Based on the eigenvectors of the subblocks (Eqs. [2] and [3]), an orthonormal eigenbasis  $\{\psi_1, \dots, \psi_8\}$  of the full mixing Hamiltonian  $\mathcal{H}_D$  can be constructed

$$\begin{aligned} \psi_1 &= |\alpha\alpha\alpha\rangle \\ \psi_2 &= \alpha_1|\beta\alpha\alpha\rangle + \beta_1|\alpha\beta\alpha\rangle + \gamma_1|\alpha\alpha\beta\rangle \\ \psi_3 &= \alpha_2|\beta\alpha\alpha\rangle + \beta_2|\alpha\beta\alpha\rangle + \gamma_2|\alpha\alpha\beta\rangle \\ \psi_4 &= \alpha_3|\beta\alpha\alpha\rangle + \beta_3|\alpha\beta\alpha\rangle + \gamma_3|\alpha\alpha\beta\rangle \\ \psi_5 &= \alpha_1|\alpha\beta\beta\rangle + \beta_1|\beta\alpha\beta\rangle + \gamma_1|\beta\beta\alpha\rangle \\ \psi_6 &= \alpha_2|\alpha\beta\beta\rangle + \beta_2|\beta\alpha\beta\rangle + \gamma_2|\beta\beta\alpha\rangle \\ \psi_7 &= \alpha_3|\alpha\beta\beta\rangle + \beta_3|\beta\alpha\beta\rangle + \gamma_3|\beta\beta\alpha\rangle \\ \psi_8 &= |\beta\beta\beta\rangle. \end{aligned} \quad [11]$$

In this eigenbasis, coherence and polarization transfer functions

$$T_{A \rightarrow B}(\tau) = \frac{\text{Tr}\{B^\dagger U(\tau) A U^\dagger(\tau)\}}{\text{Tr}\{B^\dagger B\}} \quad [12]$$

between two operators  $A$  and  $B$  can be calculated conveniently because the propagator

$$U(\tau) = \exp\{-i\mathcal{H}_D\tau\} \quad [13]$$

is diagonal with the nonzero matrix elements  $(U)_{11} = (U)_{88} = \exp\{-i\lambda_0\tau\}$ ,  $(U)_{22} = (U)_{55} = \exp\{-i\lambda_1\tau\}$ ,  $(U)_{33} = (U)_{66} = \exp\{-i\lambda_2\tau\}$  and  $(U)_{44} = (U)_{77} = \exp\{-i\lambda_3\tau\}$ . For coherence and polarization transfer functions of practical in-

**TABLE 5**  
**Polarization and Coherence Transfer Functions  $T_{A \rightarrow B}$  for Special Case 3 ( $D_{12} = D_{13} = D_{23} = D$ ) with  $A = I_{iz}$  or  $I_{ix}$**

$$\begin{aligned} T_{I_{iz} \rightarrow I_{iz}} &= T_{ii}^z = \frac{10}{18} + \frac{8}{18} \cos(3\pi D\tau) \\ T_{I_{iz} \rightarrow I_{iz}} &= T_{ik}^z = \frac{8}{18} \sin^2\left(\frac{3}{2}\pi D\tau\right) \\ T_{I_{iz} \rightarrow \{I_{ix}I_{iy} - I_{ix}I_{iy}\}} &= -\frac{2}{3} \sin(3\pi D\tau) \\ T_{I_{iz} \rightarrow \{I_{ix}I_{iy} - I_{ix}I_{iy}\}} &= 0 \\ T_{I_{iz} \rightarrow \{I_{ix}I_{ix} + I_{iy}I_{iy}\}} &= -\frac{16}{9} \sin^2\left(\frac{3}{2}\pi D\tau\right) \\ T_{I_{iz} \rightarrow \{I_{ix}I_{ix} + I_{iy}I_{iy}\}} &= \frac{8}{9} \sin^2\left(\frac{3}{2}\pi D\tau\right) \\ T_{I_{ix} \rightarrow I_{ix}} &= T_{ii}^x = \frac{7}{18} + \frac{8}{18} \cos(3\pi D\tau) + \frac{1}{6} \cos(6\pi D\tau) \\ T_{I_{ix} \rightarrow I_{ix}} &= T_{ik}^x = \frac{1}{18} - \frac{4}{18} \cos(3\pi D\tau) + \frac{1}{6} \cos(6\pi D\tau) \\ T_{I_{ix} \rightarrow I_{iz}I_{ky}} &= \frac{1}{3} \sin(6\pi D\tau) \\ T_{I_{ix} \rightarrow I_{iy}I_{kz}} &= \frac{2}{3} \sin(3\pi D\tau) + \frac{1}{3} \sin(6\pi D\tau) \\ T_{I_{ix} \rightarrow I_{jz}I_{ky}} &= -\frac{2}{3} \sin(3\pi D\tau) + \frac{1}{3} \sin(6\pi D\tau) \\ T_{I_{ix} \rightarrow I_{ix}I_{jz}I_{ky}} &= -\frac{8}{9} + \frac{8}{9} \cos(3\pi D\tau) \\ T_{I_{ix} \rightarrow I_{ix}I_{jz}I_{kz}} &= -\frac{14}{9} + \frac{8}{9} \cos(3\pi D\tau) + \frac{2}{3} \cos(6\pi D\tau) \\ T_{I_{ix} \rightarrow I_{jz}I_{jz}I_{ky}} &= \frac{8}{9} \sin^2\left(\frac{3}{2}\pi D\tau\right) \\ T_{I_{ix} \rightarrow I_{jz}I_{jz}I_{kz}} &= -\frac{2}{9} - \frac{4}{9} \cos(3\pi D\tau) + \frac{2}{3} \cos(6\pi D\tau) \end{aligned}$$

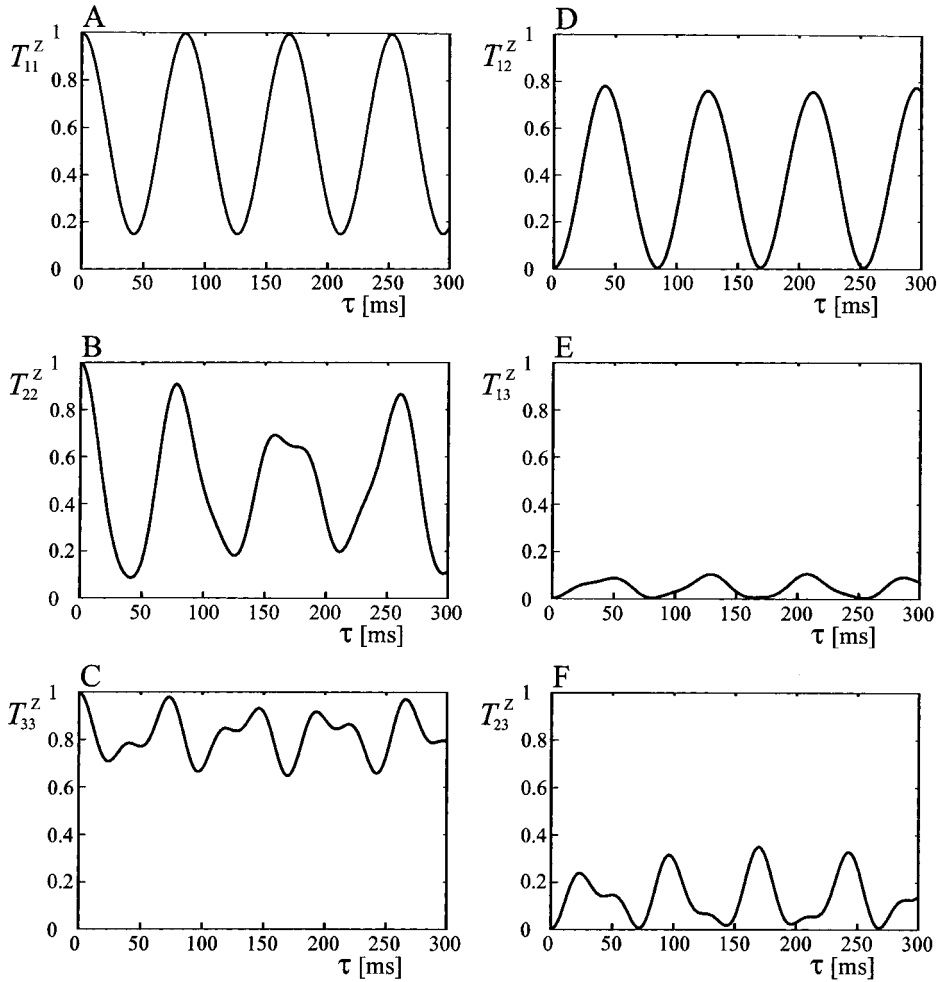
terest we were able to derive compact analytical solutions with the help of the algebraic program *Mathematica* (22).

For the initial term  $A = I_z$ , all transfer functions can be expressed as a constant term and three harmonic terms with the oscillation frequencies  $\Delta_{12}$ ,  $\Delta_{13}$ , and  $\Delta_{23}$  which correspond to differences of the eigenvalues  $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$  (cf. Eq. [5]):

$$\begin{aligned} \Delta_{12} &= \lambda_1 - \lambda_2 = -\lambda_2, \\ \Delta_{13} &= \lambda_1 - \lambda_3 = -\lambda_3, \\ \Delta_{23} &= \lambda_2 - \lambda_3 = -\pi W. \end{aligned} \quad [14]$$

For  $A = I_{iz}$ , the set of all nonzero polarization and coherence transfer functions  $T_{A \rightarrow B}$  is summarized in Table 1.

For initial magnetization  $A$  in the transverse plane (e.g.,  $A = I_x$ ), additional harmonic terms arise with oscillation frequencies



**FIG. 1.** Polarization transfer functions  $T_{kk}^z = T_{I_{kz} \rightarrow I_{kz}}$  and  $T_{kl}^z = T_{I_{kz} \rightarrow I_{lz}}$  (Table 1) for three dipolar coupled spins with coupling constants  $D_{12} = -10$  Hz,  $D_{13} = 4.6$  Hz, and  $D_{23} = 11$  Hz.

$$\Delta_{01} = \lambda_0 - \lambda_1 = \lambda_0,$$

$$\Delta_{02} = \lambda_0 - \lambda_2 = \{3\lambda_0 + \pi W\}/2,$$

$$\Delta_{03} = \lambda_0 - \lambda_3 = \{3\lambda_0 - \pi W\}/2, \quad [15]$$

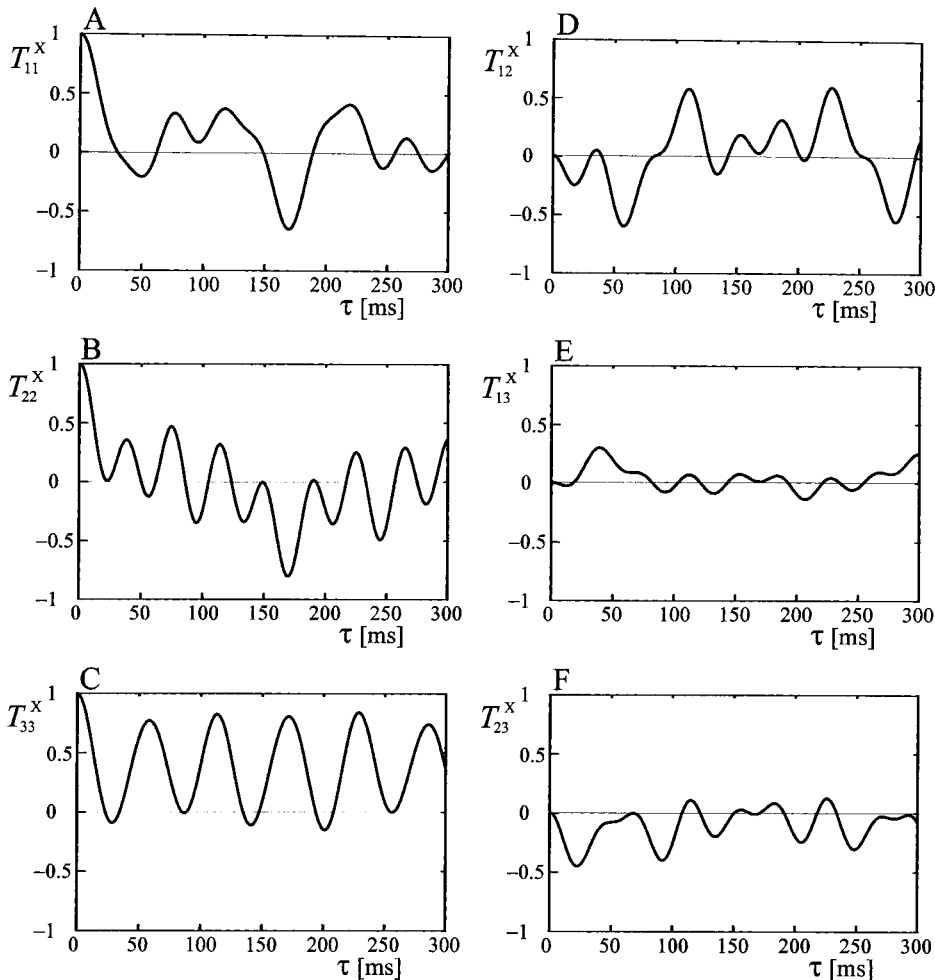
which correspond to differences of the eigenvalues of  $\mathcal{H}_D^{(\pm 1/2)}$  and  $\mathcal{H}_D^{(\pm 3/2)}$  (cf. Eqs. [2] and [3]). The set of all nonzero polarization and coherence transfer functions  $T_{A \rightarrow B}$  with  $A = I_{1x}$  are summarized in Table 2. Due to the invariance of the dipolar coupling Hamiltonian (Eq. [1]) with respect to  $z$  rotations, these transfer functions are also valid if both operators  $A$  and  $B$  are rotated by an arbitrary angle around the  $z$  axis. For example, the transfer function  $T_{I_{1x} \rightarrow I_{1z} I_{2y}}(\tau)$  is identical to  $T_{I_{1y} \rightarrow I_{1z} I_{2x}}(\tau) = -T_{I_{1y} \rightarrow I_{1z} I_{2x}}(\tau)$ .

The general transfer functions between three dipolar coupled spins (Tables 1 and 2) can be significantly simplified for symmetric spin systems. Tables 3, 4, and 5 summarize transfer functions of interest for the following three special cases: case

1 with  $D_{12} = D_{13} = D_{23}/2 = D$ , case 2 with  $D_{12} = D_{13} = D$  and  $D_{23} = 0$ , and case 3 with  $D_{12} = D_{13} = D_{23} = D$ .

## TRANSFER EFFICIENCY

In Figs. 1 and 2, representative transfer functions are shown for the general case of three dipolar coupled spins without permutation symmetry. The analytical transfer functions are identical to simulated transfer functions that were calculated numerically using the program package SIMONE (23) (data not shown). Dipolar coupling constants  $D_{12} = -10$  Hz,  $D_{13} = 4.6$  Hz, and  $D_{23} = 11$  Hz were chosen to match the coupling constants for which transfer functions have been presented previously for isotropic (7) and planar (17) mixing conditions. This allows for a direct comparison of the markedly different transfer dynamics in a dipolar coupled spin system versus isotropically or planar coupled spins. For this particular set of coupling constants, the dipolar transfer of  $z$  magnetization is



**FIG. 2.** Coherence transfer functions  $T_{ik}^x = T_{I_{k\alpha} \rightarrow I_{i\alpha}}$  and  $T_{kl}^x = T_{I_{l\alpha} \rightarrow I_{k\alpha}}$  (Table 2) for three dipolar coupled spins with coupling constants  $D_{12} = -10$  Hz,  $D_{13} = 4.6$  Hz, and  $D_{23} = 11$  Hz.

most efficient between spins 1 and 2 (Fig. 1D), whereas very little magnetization is transferred between spins 1 and 3 (Fig. 1F). This is in contrast to the case of planar mixing, where the most efficient transfer is found between spins 1 and 3 and the transfer between spins 1 and 2 is the least efficient (17). A comparison of Figs. 1 and 2 shows that for some spin pairs the transfer of  $z$  magnetization can be superior to the transfer of  $x$  magnetization (cf. Figs. 1D and 2D) while for others the transfer of  $x$  magnetization is more efficient (cf. Figs. 1E and 2E).

A global picture of the dependence of the transfer efficiency on the relative size of the coupling constants  $D_{12}$ ,  $D_{13}$ , and  $D_{23}$  can be obtained with the help of a quality factor that reflects both the transfer time and the transfer amplitude between two operators  $I_{k\alpha}$  and  $I_{l\alpha}$ . Such a quality factor is the so-called direct transfer efficiency, defined as

$$\eta_{kl}^{\alpha} = s \max_{\tau > 0} \{ |T_{I_{k\alpha} \rightarrow I_{l\alpha}}(\tau)| \exp(-\tau |D_{kl}|) \}, \quad [16]$$

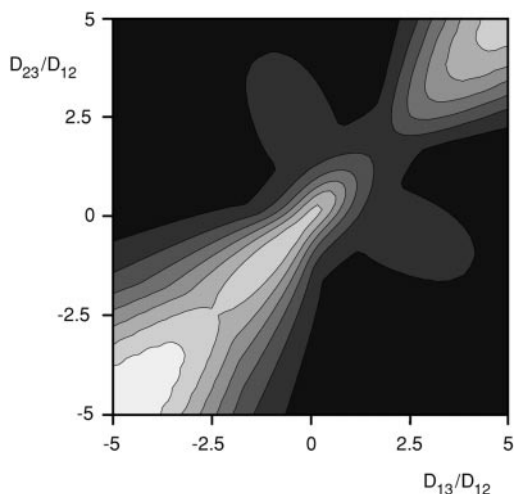
where  $s$  is 1 (or  $-1$ ) if  $T_{I_{k\alpha} \rightarrow I_{l\alpha}}(\tau_{max})$  is positive (or negative) at the mixing time  $\tau_{max}$  where  $|T_{I_{k\alpha} \rightarrow I_{l\alpha}}(\tau)| \exp(-\tau |D_{kl}|)$  assumes its maximum value. Equation [16] is a straightforward generalization of the original definition of the direct transfer efficiency (3, 24) to include the case of negative transfer functions. In Figs. 3 and 4,  $\eta_{12}^z$  and  $\eta_{12}^x$  are shown as a function of the relative dipolar coupling constants  $D_{13}/D_{12}$  and  $D_{23}/D_{12}$ . As the dipolar coupling Hamiltonian of Eq. [1] is invariant under  $z$  rotations,  $\eta_{12}^y = \eta_{12}^x$ . The most efficient transfer of  $z$  magnetization between spins 1 and 2 is found if  $D_{13} \approx D_{23} > 3D_{12}$  or if  $D_{13} \approx D_{23} < D_{12}$  (cf. Fig. 3). In particular, the transfer between spins 1 and 2 is quenched if  $D_{13}$  and  $D_{23}$  have opposite signs and  $|D_{13}| \approx |D_{23}| > |D_{12}|$ . This is the case for the transfer shown in Fig. 1E if the spin labels are permuted such that two spins between which polarization transfer is considered are labeled 1 and 2. As can be seen in Fig. 3, there are many other combinations of coupling constants for which polarization transfer between two spins can be very weak even



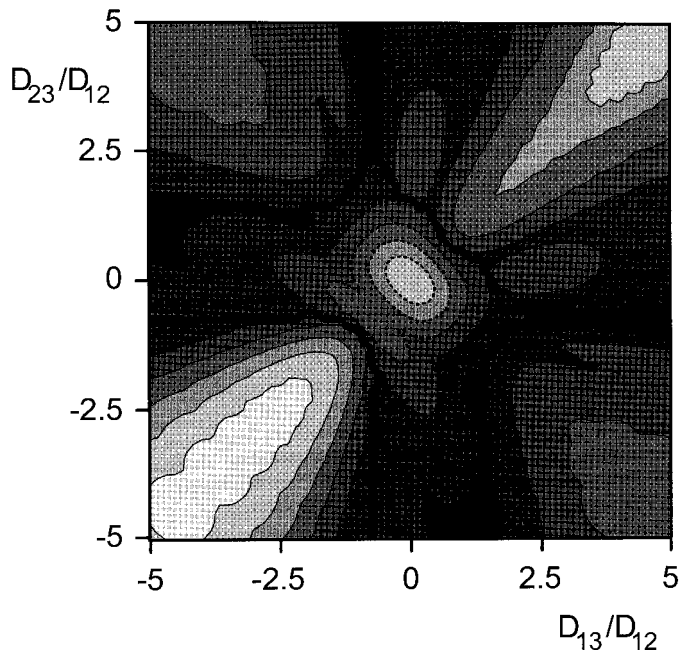
if large dipolar couplings exist between these spins. This finding will be important for the correct interpretation of experimental DCOSY spectra. A more complex dependence of the size and sign of the direct transfer efficiency is found for the transfer of  $x$  magnetization (cf. Fig. 4). As expected, the transfer efficiency can be either positive or negative. Note that in contrast to the transfer of  $z$  magnetization, significant transfer of  $x$  magnetization occurs if  $D_{13}$  and  $D_{23}$  have opposite signs and  $|D_{13}| \approx |D_{23}| > |D_{12}|$ . Hence, in some cases, the quenching of polarization transfer can be circumvented by transferring  $x$  rather than  $z$  magnetization. Corresponding transfer efficiency maps with a significantly different dependence on the relative size of the coupling constants have been published previously for the case of isotropic and planar mixing (3, 24).

## DISCUSSION

Coherence and polarization transfer functions were derived for a general spin system consisting of three dipolar coupled spins with the Hamiltonian given in Eq. [1]. In the mixing period of DCOSY experiments (18), WALTZ-16 (25), and DIPSI-2 (26) sequences can be used in order to create energy matched conditions. Similar to  $CW_x$  irradiation, these sequences create effective coupling terms that have the form of Eq. [1]. However, the unique axis of quantization is changed from  $z$  to  $x$  and the coupling constants are scaled by a factor of  $-\frac{1}{2}$  (27). Hence, the derived analytical solutions are also valid for the transfer under these mixing sequences if the axis labels  $\{x, y, z\}$  are replaced by  $\{y, z, x\}$  and if the dipolar coupling constants  $D_{kl}$  are replaced by  $D_{kl,eff} = -D_{kl}/2$ . A detailed analysis of the offset dependence of the effective Hamiltonian created by DCOSY sequences is given in (28).



**FIG. 3.** Polarization transfer efficiency map  $\eta_{i2}^z$  (Eq. [16]) as a function of the relative dipolar coupling constants  $D_{13}/D_{12}$  and  $D_{23}/D_{12}$ . Regions where  $\eta_{i2}^z < 0.1$  are black. The level increment is 0.1.



**FIG. 4.** Coherence transfer efficiency map  $\eta_{i2}^x$  (Eq. [16]) as a function of the relative dipolar coupling constants  $D_{13}/D_{12}$  and  $D_{23}/D_{12}$ . Regions where  $|\eta_{i2}^x| < 0.1$  are black. Positive and negative contour levels are drawn as solid and dashed lines. The level increment is 0.1.

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