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Superposition of Scalar and Residual Dipolar Couplings: Analytical Transfer Functions for Three Spins 1/2 under Cylindrical Mixing Conditions

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The superposition of scalar and residual dipolar couplings gives rise to so-called cylindrical mixing Hamiltonians in dipolar coupling spectroscopy. General analytical polarization and coherence transfer functions are presented for three cylindrically coupled spins $\frac{1}{2}$ under energy-matched conditions. In addition, the transfer efficiency is analyzed as a function of the relative coupling constants for characteristic special cases.

Key Words: **Hartmann–Hahn transfer; residual dipolar couplings; analytical transfer functions; TOCSY; DCOSY.**

INTRODUCTION

Homonuclear and heteronuclear coherence and polarization transfer under energy-matched conditions is an important tool in both liquid and solid state NMR (*1–9*). Such homonuclear and heteronuclear Hartmann–Hahn type experiments can be classified according to the form of the coupling tensors in the effective mixing Hamiltonian (*9, 10*). For example, isotropic coupling tensors are created by heteronuclear isotropic mixing sequences (*9, 11, 12*) and by most homonuclear Hartmann–Hahn sequences if applied to scalar coupled spin systems (*5, 6, 9*). Effective planar coupling tensors (*13*) are typical for most heteronuclear Hartmann–Hahn experiments (*1, 7, 9*) and for homonuclear Hartmann–Hahn experiments that are based on RF irradiation at multiple frequencies (*14–19*). Recently, residual dipolar couplings of partially ordered systems have found wide use in high-resolution NMR of biomolecules (*20–23*). The simultaneous presence of isotropic couplings and residual dipolar couplings can give rise to a large variety of effective coupling tensors.

In principle, polarization and coherence transfer functions that describe the dynamics of polarization and coherence transfer can be simulated numerically for arbitrary coupling tensors (*8, 9, 24–31*). However, analytical transfer functions are also highly desirable in order to understand the characteristic transfer dynamics. For a two-spin system, analytical coherence and polarization transfer functions are known for a large range of practically relevant effective coupling tensors (*9, 23, 32, 33*). For three-spin systems with arbitrary coupling constants, analytical transfer functions have been derived for isotropic, planar, and dipolar effective coupling tensors (*19, 34, 35*). For spin systems consisting of four coupled spins 1/2 with arbitrary coupling constants, analytical transfer functions are only known for isotropic mixing experiments (*36, 37*). In homonuclear Hartmann–Hahn experiments of partially oriented samples (*23*), the size of scalar coupling constants is typically of the same order of magnitude as the size of the residual dipolar couplings. The class of effective coupling tensors created by the simultaneous presence of isotropic and dipolar couplings corresponds to the anisotropic Ising–Heisenberg model (*38*) and has also been denoted cylindrical coupling (*33*). For two cylindrically coupled spins 1/2, the derivation of analytical transfer functions (*9, 23, 33*) is relatively simple because all terms of the coupling Hamiltonian mutually commute. However, this is not the case for more than two cylindrically coupled spins. In the following, analytical polarization and coherence transfer functions are presented for spin systems consisting of three spins 1/2 under general cylindrical mixing condition with arbitrary coupling constants. In addition, the efficiency of polarization and coherence transfer is analyzed for a number of characteristic coupling topologies.

TWO-SPIN CASE

For a two-spin system the anisotropic Ising–Heisenberg (*38*) or cylindrical (*33*) coupling term can be expressed in the form (*10*)

$$\mathcal{H}_{\text{cyl}} = 2\pi J^{\text{P}}(I_xS_x + I_yS_y) + 2\pi J^{\text{L}}I_zS_z, \qquad [1]$$

with the planar and longitudinal coupling constants J^{P} and J^{L}, respectively. For $J^{\text{P}} = 0$ Eq. [1] reduces to the longitudinal coupling term $2\pi J^{\text{L}}I_zS_z$ (*9, 10*) that is characteristic for the weak coupling limit and that corresponds to the coupling term of the standard Ising model Hamiltonian (*38–40*). For $J^{\text{L}} = 0$ the coupling term $\mathcal{H}_{\text{cyl}}$ represents a planar mixing Hamiltonian (*9, 10, 13*) which corresponds to the coupling terms in the *XY* model (*42*). For $J^{\text{L}} = J^{\text{P}}$ the coupling term $\mathcal{H}_{\text{cyl}}$ represents an

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isotropic mixing Hamiltonian (*5, 9, 11, 12*) which corresponds to the coupling term in the Heisenberg or Heisenberg–Dirac–Van Vleck model Hamiltonian (*41, 43*). For $J^{L} = -2J^{P}$ the Hamiltonian $\mathcal{H}_{cyl}$ represents a dipolar coupling term (*44*).

The combination of an (effective) isotropic coupling term $\mathcal{H}_{iso} = 2\pi J\{I_xS_x + I_yS_y + I_zS_z\}$ and an (effective) dipolar coupling term of the form $\mathcal{H}_{dip} = 2\pi D\{2I_zS_z - I_xS_x - I_yS_y\}$ also results in a cylindrical mixing Hamiltonian $\mathcal{H}_{cyl}$ in the form of Eq. [1] with

$$J^{L} = J + 2D, \quad J^{P} = J - D. \qquad [2]$$

For a two-spin system the coherence and polarization transfer functions for cylindrical mixing can be derived in a straightforward way (*9, 23, 33*). A summary of the relevant transfer functions using the above nomenclature is given in Table 1. For a longitudinal initial operator $A = I_z$, the transfer functions are independent of the longitudinal coupling constant J^{L} because the coupling term $2\pi J^{L}I_zS_z$ commutes both with I_z and with $2\pi J^{P}$ $(I_xS_x + I_yS_y)$. On the other hand, transfer functions for the transverse initial operators $A = I_x$ or I_y depend on both J^{P} and J^{L}. This is illustrated in Fig. 1 where characteristic transfer functions $T_{I_z\to S_z}$ and $T_{I_x\to S_x}$ are shown.

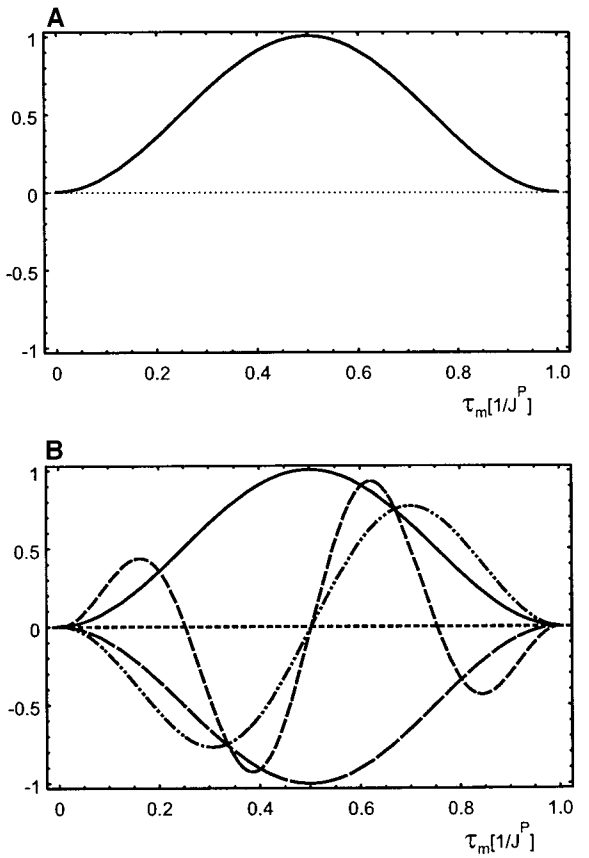

FIG. 1. Polarization and coherence transfer functions of a two-spin system under various cylindrical mixing conditions (see Eq. [1]). (A) The polarization transfer function $T_{I_z\to S_z}$ is independent of J^{L} and only depends on the planar coupling constant J^{P}. (B) In contrast, the coherence transfer functions $T_{I_x\to S_x} = T_{I_y\to S_y}$ depend not only on J^{P} but also on J^{L}. The curves represent characteristic coherence transfer functions for $J^{L} = -2J^{P}$ (dipolar mixing, – - - –), $J^{L} = -J^{P}$ (— — —), $J^{L} = 0$ (planar mixing, - - -), $J^{L} = J^{P}$ (isotropic mixing, —), and $J^{L} = 4J^{P}$ (– – –).

THREE-SPIN CASE

For a spin system consisting of three coupled spins 1/2, the anisotropic Ising–Heisenberg or cylindrical mixing Hamiltonian has the form

$$\mathcal{H}_{cyl} = 2\pi \sum_{i<j}^{3} J_{ij}^{P}\{I_{ix}I_{jx} + I_{iy}I_{jy}\} + 2\pi \sum_{i<j}^{3} J_{ij}^{L}I_{iz}I_{jz}, \qquad [3]$$

with the effective planar and longitudinal coupling constants J_{ij}^{P} and J_{ij}^{L}, respectively. In analogy to the case of three coupled spins under planar or dipolar mixing conditions, polarization transfer functions can be determined if the eigenvalues and eigenfunctions of $\mathcal{H}_{cyl}$ are known (*19, 35*). As $\mathcal{H}_{cyl}$ commutes with $F_z = I_{1z} + I_{2z} + I_{3z}$, the mixing Hamiltonian assumes a block structure in the basis of the product functions $|\alpha\alpha\alpha\rangle$ (with magnetic quantum number $m = 3/2$), $|\beta\alpha\alpha\rangle$, $|\alpha\beta\alpha\rangle$, $|\alpha\alpha\beta\rangle$ (with $m = 1/2$), $|\alpha\beta\beta\rangle$, $|\beta\alpha\beta\rangle$, $|\beta\beta\alpha\rangle$ (with $m = -1/2$), and $|\beta\beta\beta\rangle$ (with $m = -3/2$). Each block only connects product functions with equal magnetic quantum number m. For $m = \pm 3/2$, the resulting 1×1 blocks are

$$\mathcal{H}_{cyl}^{(3/2)} = \mathcal{H}_{cyl}^{(-3/2)} = \frac{\pi}{2}\,(J_{12}^{L} + J_{13}^{L} + J_{23}^{L}) = \lambda_0, \qquad [4]$$

where λ_0 corresponds to two degenerate eigenvalues of $\mathcal{H}_{cyl}$. For $m = \pm 1/2$, the blocks have the form

$$\mathcal{H}_{cyl}^{(1/2)} = \mathcal{H}_{cyl}^{(-1/2)} = \pi\begin{pmatrix} \Sigma_1 & J_{12}^{P} & J_{13}^{P} \\ J_{12}^{P} & \Sigma_2 & J_{23}^{P} \\ J_{13}^{P} & J_{23}^{P} & \Sigma_3 \end{pmatrix}, \qquad [5]$$

TABLE 1
Coherence and Polarization Transfer Functions $T_{A\to B}$ for Two Spins I and S under Cylindrical Mixing Conditions

$$T_{I_x\to I_x} = T_{I_y\to I_y} = 1 - \sin(\pi J^{L}\tau)\sin(\pi J^{P}\tau)$$
$$T_{I_z\to I_z} = 1 - \sin^2(\pi J^{P}\tau)$$
$$T_{I_x\to S_x} = T_{I_y\to S_y} = \sin(\pi J^{L}\tau)\sin(\pi J^{P}\tau)$$
$$T_{I_z\to S_z} = \sin^2(\pi J^{P}\tau)$$
$$T_{I_y\to 2I_xS_z} = -T_{I_x\to 2I_yS_z} = \frac{1}{2}\{\sin(\pi(J^{L} + J^{P})\tau) + \sin(\pi(J^{L} - J^{P})\tau)\}$$
$$T_{I_x\to 2I_zS_y} = -T_{I_y\to 2I_zS_x} = \frac{1}{2}\{\sin(\pi(J^{L} + J^{P})\tau) - \sin(\pi(J^{L} - J^{P})\tau)\}$$
$$T_{I_z\to 2I_yS_x} = -T_{I_z\to 2I_xS_y} = \frac{1}{2}\sin(2\pi J^{P}\tau)$$

with

$$\Sigma_i = \frac{J^{\mathrm{L}}_{jk} - J^{\mathrm{L}}_{ij} - J^{\mathrm{L}}_{ik}}{2} \qquad [6]$$

for $\{ijk\} = \{123\}$, $\{231\}$, and $\{312\}$ and with $J^{\mathrm{L}}_{ij} = J^{\mathrm{L}}_{ji}$ and $J^{\mathrm{P}}_{ij} = J^{\mathrm{P}}_{ji}$. The eigenvalues of these 3×3 matrices can be found using Cardan's formula (*45*):

$$\lambda_1 = -\frac{\lambda_0}{3} + 4\pi\sqrt{\frac{|p|}{3}}\cos\left(\frac{\varphi}{3}\right)$$

$$\lambda_{2,3} = -\frac{\lambda_0}{3} - 4\pi\sqrt{\frac{|p|}{3}}\cos\left(\frac{\varphi \mp \pi}{3}\right), \qquad [7]$$

with

$$\varphi = \arccos\left(\frac{-q}{2\sqrt{\frac{|p|}{3}}^3}\right), \qquad [8]$$

$$p = \frac{1}{12}\sum_{i<j}^{3}\Sigma_i\Sigma_j - (\Sigma_i)^2 - 3(J^{\mathrm{P}}_{ij})^2$$

and

$$q = \frac{1}{3}\left\{J^{\mathrm{P}}_{12}\Sigma_3 + J^{\mathrm{P}}_{13}\Sigma_2 + J^{\mathrm{P}}_{23}\Sigma_1 - \frac{1}{4}J^{\mathrm{P}}_{12}J^{\mathrm{P}}_{13}J^{\mathrm{P}}_{23} - \frac{1}{3}\Sigma_1\Sigma_2\Sigma_3 + \sum_{i\neq j}^{3}\Sigma_i\left(\frac{8}{3}\Sigma_i\Sigma_j - \frac{1}{2}J^{\mathrm{P}}_{ij}\right) - \frac{1}{36}\sum_{i}^{3}(\Sigma_i)^3\right\}. \qquad [9]$$

For each eigenvalue λ_i (Eq. [7]) the three components α_i, β_i, and γ_i of the corresponding normalized eigenvectors are given by

$$\alpha_i = c_i^{(123)}/n_i, \quad \beta_i = c_i^{(231)}/n_i, \quad \gamma_i = c_i^{(312)}/n_i, \qquad [10]$$

with

$$c_i^{(lmn)} = J^{\mathrm{P}}_{mn}(J^{\mathrm{P}}_{mn} - J^{\mathrm{P}}_{lm} - J^{\mathrm{P}}_{ln}) - \Sigma_m\Sigma_n + \Sigma_m J^{\mathrm{P}}_{ln} + \Sigma_n J^{\mathrm{P}}_{lm} + (\Sigma_m - J^{\mathrm{P}}_{lm} + \Sigma_n - J^{\mathrm{P}}_{ln})(\lambda_i/\pi) - (\lambda_i/\pi)^2 \qquad [11]$$

and

$$n_i = \sqrt{(c_i^{(123)})^2 + (c_i^{(231)})^2 + (c_i^{(312)})^2}. \qquad [12]$$

In special cases (e.g., for isotropic mixing with $J^{\mathrm{P}}_{ij} = J^{\mathrm{L}}_{ij}$) when $c_1^{(lmn)} = c_2^{(lmn)} = c_3^{(lmn)} = 0$ for all combinations (lmn), Eq. [11] is to be replaced by

$$c_i^{(123)} = \Sigma_2 J^{\mathrm{P}}_{13} - J^{\mathrm{P}}_{12}J^{\mathrm{P}}_{23} - J^{\mathrm{P}}_{13}(\lambda_i/\pi)$$

$$c_i^{(231)} = \Sigma_1 J^{\mathrm{P}}_{23} - J^{\mathrm{P}}_{12}J^{\mathrm{P}}_{13} - J^{\mathrm{P}}_{23}(\lambda_i/\pi)$$

$$c_i^{(312)} = (J^{\mathrm{P}}_{12})^2 - \Sigma_1\Sigma_2 + (\Sigma_1 + \Sigma_2)(\lambda_i/\pi) - (\lambda_i/\pi)^2. \qquad [13]$$

Equations [10]–[13] represent the eigenvector components in all cases where the eigenvalues (Eq. [7]) are nondegenerate i.e., $\lambda_1 \neq \lambda_2 \neq \lambda_3 \neq \lambda_1$. In the practical calculation of transfer functions this can always be achieved by a slight variation of the coupling constants. Based on the components of the eigenvectors (Eq. [10]), an orthonormal eigenbasis of the mixing Hamiltonian $\mathcal{H}_{\mathrm{cyl}}$ is given by

$$\begin{aligned}
\psi_1 &= |\alpha\alpha\alpha\rangle \\
\psi_2 &= \alpha_1|\beta\alpha\alpha\rangle + \beta_1|\alpha\beta\alpha\rangle + \gamma_1|\alpha\alpha\beta\rangle \\
\psi_3 &= \alpha_2|\beta\alpha\alpha\rangle + \beta_2|\alpha\beta\alpha\rangle + \gamma_2|\alpha\alpha\beta\rangle \\
\psi_4 &= \alpha_3|\beta\alpha\alpha\rangle + \beta_3|\alpha\beta\alpha\rangle + \gamma_3|\alpha\alpha\beta\rangle \\
\psi_5 &= \alpha_1|\alpha\beta\beta\rangle + \beta_1|\beta\alpha\beta\rangle + \gamma_1|\beta\beta\alpha\rangle \\
\psi_6 &= \alpha_2|\alpha\beta\beta\rangle + \beta_2|\beta\alpha\beta\rangle + \gamma_2|\beta\beta\alpha\rangle \\
\psi_7 &= \alpha_3|\alpha\beta\beta\rangle + \beta_3|\beta\alpha\beta\rangle + \gamma_3|\beta\beta\alpha\rangle \\
\psi_8 &= |\beta\beta\beta\rangle.
\end{aligned} \qquad [14]$$

In this eigenbasis, transfer functions

$$T_{A\to B}(\tau) = \frac{\mathrm{Tr}\{B^\dagger U(\tau) A U^\dagger(\tau)\}}{\mathrm{Tr}\{B^\dagger B\}} \qquad [15]$$

between two operators A and B can be calculated in a straightforward way because the propagator

$$U(\tau) = \exp\{-i\mathcal{H}_{\mathrm{cyl}}\tau\} \qquad [16]$$

is diagonal with $(U)_{11} = (U)_{88} = \exp\{-i\lambda_0\tau\}$, $(U)_{22} = (U)_{55} = \exp\{-i\lambda_1\tau\}$, $(U)_{33} = (U)_{66} = \exp\{-i\lambda_2\tau\}$, and $(U)_{44} = (U)_{77} = \exp\{-i\lambda_3\tau\}$.

With the help of the algebraic program *Mathematica* (*46*) we derived compact analytical expressions for coherence and polarization transfer functions of practical interest. All nonzero polarization and coherence transfer functions $T_{A\to B}$ for $A = I_{1z}$ and $A = I_{1x}$ are summarized in Tables 2 and 3, respectively. As the cylindrical mixing Hamiltonian is invariant under rotations around the z axis, the transfer functions $T_{I_{1x}\to B}$ are identical to the transfer functions $T_{I_{1y}\to B'}$, where the target operator B' is

TABLE 2
Polarization Transfer Functions $T_{I_{1z}\to B}$ for a Three-Spin System under Cylindrical Mixing Conditions

$$T_{I_{1z}\to I_{1z}} = T^z_{11} = 1 - \sum_{i<j}^{3} \frac{1}{2} w_{ij}^2\{1 - \cos(\Delta_{ij}\tau)\}$$

$$T_{I_{1z}\to I_{2z}} = T^z_{12} = \sum_{i<j}^{3} \frac{1}{2}\{(\alpha_i\alpha_j - \beta_i\beta_j)^2 - (\gamma_i\gamma_j)^2\}(1 - \cos(\Delta_{ij}\tau)\}$$

$$T_{I_{1z}\to I_{3z}} = T^z_{12} = \sum_{i<j}^{3} \frac{1}{2}\{(\alpha_i\alpha_j - \gamma_i\gamma_j)^2 - (\beta_i\beta_j)^2\}\{1 - \cos(\Delta_{ij}\tau)\}$$

$$T_{I_{1z}\to I_{1x}I_{2y}-I_{2x}I_{1y}} = \sum_{i<j}^{3} \frac{1}{2}\{(\beta_i\alpha_j - \alpha_i\beta_j)w_{ij}\}\sin(\Delta_{ij}\tau)$$

$$T_{I_{1z}\to I_{1x}I_{3y}-I_{3x}I_{1y}} = \sum_{i<j}^{3} \frac{1}{2}\{(\gamma_i\alpha_j - \alpha_i\gamma_j)w_{ij}\}\sin(\Delta_{ij}\tau)$$

$$T_{I_{1z}\to I_{2x}I_{3y}-I_{3x}I_{2y}} = \sum_{i<j}^{3} \frac{1}{2}\{(\gamma_i\beta_j - \beta_i\gamma_j)w_{ij}\}\sin(\Delta_{ij}\tau)$$

$$T_{I_{1z}\to I_{1z}(I_{2x}I_{3x}+I_{2y}I_{3y})} = \sum_{i<j}^{3} \frac{1}{4}\{(\beta_i\gamma_j + \gamma_i\beta_j)w_{ij}\}\{1 - \cos(\Delta_{ij}\tau)\}$$

$$T_{I_{1z}\to I_{2z}(I_{1x}I_{3x}+I_{1y}I_{3y})} = \sum_{i<j}^{3} \frac{1}{4}\{(\alpha_i\gamma_j + \gamma_i\alpha_j)w_{ij}\}\{1 - \cos(\Delta_{ij}\tau)\}$$

$$T_{I_{1z}\to I_{3z}(I_{1x}I_{2x}+I_{1y}I_{2y})} = \sum_{i<j}^{3} \frac{1}{4}\{(\alpha_i\beta_j + \beta_i\alpha_j)w_{ij}\}\{1 - \cos(\Delta_{ij}\tau)\}$$

Note. α_i, β_i, and γ_i are defined in Eq. [10] and $w_{ij} = \alpha_i\alpha_j - \beta_i\beta_j - \gamma_i\gamma_j$.

related to B by a 90° z rotation. Except for constant terms, all polarization transfer functions $T_{I_{kz}\to B}$ can be expressed as combinations of three harmonic terms with oscillation frequencies Δ_{12}, Δ_{13}, and Δ_{23} corresponding to differences of the eigenvalues λ_1, λ_2, and λ_3 (c.f. Eq. [7]):

$$\Delta_{ij} = \lambda_i - \lambda_j. \qquad [17]$$

In the transfer functions $T_{I_{k\alpha}\to B}$ of transverse magnetization, three additional harmonic terms occur with oscillation frequencies $\Delta_{0i} = \lambda_0 - \lambda_i$ with $i = 1$, 2, and 3 (c.f. Eqs. [4] and [7]).

TRANSFER EFFICIENCIES

Examples of characteristic transfer functions $T_{I_z\to B}$ and $T_{I_x\to B}$ are shown in Figs. 2 and 3, respectively. As in Fig. 1, the ratio $J^{\mathrm{L}}_{ij}/J^{\mathrm{P}}_{ij}$ of longitudinal and planar coupling constants was varied between -2 (A–A″) and 4 (F–F″). The planar coupling constants were chosen to be $J^{\mathrm{P}}_{12} = -10$ Hz, $J^{\mathrm{P}}_{13} = 4.6$ Hz, and $J^{\mathrm{P}}_{23} = 11$ Hz in order to simplify the comparison with previously presented theoretical (*19*, *34*, *35*) and experimental (*19*, *34*) transfer functions. The analytical transfer functions are identical to simulated transfer functions that were calculated numerically using the program SIMONE (*29*) (data not shown).

In contrast to the case of two cylindrically coupled spins (cf. Fig. 1A), the transfer of polarization $T_{I_{kz}\to I_{lz}}$ does depend on the ratio $J^{\mathrm{L}}_{ij}/J^{\mathrm{P}}_{ij}$ of longitudinal and planar coupling constants in the case of three coupled spins (cf. Fig. 2), because the planar and longitudinal coupling terms only commute in the case of two coupled spins but not in the case of three coupled spins. The coherence transfer functions $T_{I_{kx}\to I_{lx}}$ (see Fig. 3 and Table 3) are in general more complicated than the corresponding polarization transfer functions $T_{I_{kz}\to I_{lz}}$ (see Fig. 2 and Table 2). Whereas only positive polarization transfer functions $T_{I_{kz}\to I_{lz}}$ are found for three cylindrically coupled spins 1/2, the coherence transfer functions $T_{I_{kx}\to I_{lx}}$ can also become negative, except for the case of isotropic mixing where $T_{I_{kx}\to I_{lx}} = T_{I_{kz}\to I_{lz}}$ is always positive (*24*, *34*, *47*).

In order to introduce a concise notation for the discussion of the transfer efficiency under various combinations of cylindrical coupling tensors, we rewrite $\mathcal{H}_{\mathrm{cyl}}$ (Eq. [3]) in the form (*10*).

$$\mathcal{H}_{\mathrm{cyl}} = 2\pi \sum_{i<j}^{3} J_{ij}\{s^{\mathrm{P}}_{ij}(I_{ix}I_{jx} + I_{iy}I_{jy}) + s^{\mathrm{L}}_{ij}I_{iz}I_{jz}\}, \qquad [18]$$

where the planar and longitudinal coupling constants are related to the fictitious coupling constants J_{ij} by $J^{\mathrm{P}}_{ij} = s^{\mathrm{P}}_{ij}J_{ij}$ and $J^{\mathrm{L}}_{ij} = s^{\mathrm{L}}_{ij}J_{ij}$, respectively. In analogy to previous definitions (*9*, *10*, *35*) of quality factors that reflect both the amplitude and the duration of the transfer from $I_{k\alpha}$ to $I_{l\alpha}$, we define the transfer efficiency η^{α}_{kl} for cylindrical mixing as

$$\eta^{\alpha}_{kl} = \kappa \max_{\tau>0}\{|T_{I_{k\alpha}\to I_{l\alpha}}(\tau)|\exp(-\tau|J_{kl}|)\}, \qquad [19]$$

where κ is 1 (or -1) if $T_{I_{k\alpha}\to I_{l\alpha}}(\tau_{\max})$ is positive (or negative) at the mixing time $\tau_{\max}$ where $|T_{I_{k\alpha}\to I_{l\alpha}}(\tau)|\exp(-\tau|J_{kl}|)$ assumes its maximum value. For a given set of planar and longitudinal scaling factors $\mathbf{s}^{\mathrm{P}} = \{s^{\mathrm{P}}_{12}, s^{\mathrm{P}}_{13}, s^{\mathrm{P}}_{23}\}$ and $\mathbf{s}^{\mathrm{L}} = \{s^{\mathrm{L}}_{12}, s^{\mathrm{L}}_{13}, s^{\mathrm{L}}_{23}\}$ the transfer efficiency η^{α}_{12} depends only on the relative coupling constants J_{13}/J_{12} and J_{23}/J_{12}, which makes it possible to plot two-dimensional transfer efficiency maps $\eta^{\alpha}_{12}(J_{13}/J_{12}, J_{23}/J_{12})$ (*10*).

Figures 4 and 5 show longitudinal and transverse transfer efficiency maps η^{z}_{12} and $\eta^{x}_{12} = \eta^{y}_{12}$ for a number of characteristic sets of scaling factors $\mathbf{s}^{\mathrm{P}}$ and $\mathbf{s}^{\mathrm{L}}$. Figures 4A and 5A correspond to the case of isotropic mixing for a two-spin system where $\eta^{z}_{12} = \eta^{x}_{12} = 0.62$ (*10*). In Figs. 4B and 5B, spins 1 and 2 are isotropically coupled whereas spin pairs 1–3 and 2–3 have a purely longitudinal coupling tensor (*10*). Figures 4C and 5C represent an intermediate case between Figs. 4B and 5B and the case where all three spins are isotropically coupled (Figs. 4E and 5E). Figures 4D–4L and 5D–5L represent a series of longitudinal and transverse transfer efficiency

TABLE 3
Coherence Transfer Functions $T_{I_{1x}\rightarrow B}$ for a Three-Spin System under Cylindrical Mixing Conditions

$$T_{I_{1x}\rightarrow I_{1x}} = T_{11}^{x} = \sum_{i=1}^{3} \gamma_i^2\beta_i^2 + \frac{1}{2}\sum_{i=1}^{3} \alpha_i^2 \cos(\Delta_{0i}\tau) + \frac{1}{2}\sum_{i=1}^{3}\sum_{j=i+1}^{3} \nu_{ij}^2 \cos(\Delta_{ij}\tau)$$

$$T_{I_{1x}\rightarrow I_{2x}} = T_{12}^{x} = \sum_{i=1}^{3} \gamma_i^2\beta_i\alpha_i + \frac{1}{2}\sum_{i=1}^{3} \beta_i\alpha_i\cos(\Delta_{0i}\tau) + \frac{1}{2}\sum_{i=1}^{3}\sum_{j=i+1}^{3} \nu_{ij}(\gamma_i\alpha_j + \gamma_j\alpha_i)\cos(\Delta_{ij}\tau)$$

$$T_{I_{1x}\rightarrow I_{3x}} = T_{13}^{x} = \sum_{i=1}^{3} \gamma_i\beta_i^2\alpha_i + \frac{1}{2}\sum_{i=1}^{3} \gamma_i\alpha_i\cos(\Delta_{0i}\tau) + \frac{1}{2}\sum_{i=1}^{3}\sum_{j=i+1}^{3} \nu_{ij}(\beta_i\alpha_j + \beta_j\alpha_i)\cos(\Delta_{ij}\tau)$$

$$T_{I_{1x}\rightarrow I_{1z}I_{2y}} = \sum_{i=1}^{3} \beta_i\alpha_i\sin(\Delta_{0i}\tau) + \sum_{i=1}^{3}\sum_{j=i+1}^{3} \nu_{ij}(\gamma_i\alpha_j - \gamma_j\alpha_i)\sin(\Delta_{ij}\tau)$$

$$T_{I_{1x}\rightarrow I_{2z}I_{1y}} = \sum_{i=1}^{3} \alpha_i^2\sin(\Delta_{0i}\tau) + \sum_{i=1}^{3}\sum_{j=i+1}^{3} \nu_{ij}(\gamma_i\beta_j - \gamma_j\beta_i)\sin(\Delta_{ij}\tau)$$

$$T_{I_{1x}\rightarrow I_{1z}I_{3y}} = \sum_{i=1}^{3} \gamma_i\alpha_i\sin(\Delta_{0i}\tau) + \sum_{i=1}^{3}\sum_{j=i+1}^{3} \nu_{ij}(\beta_i\alpha_j - \beta_j\alpha_i)\sin(\Delta_{ij}\tau)$$

$$T_{I_{1x}\rightarrow I_{3z}I_{1y}} = \sum_{i=1}^{3} \alpha_i^2\sin(\Delta_{0i}\tau) - \sum_{i=1}^{3}\sum_{j=i+1}^{3} \nu_{ij}(\gamma_i\beta_j - \gamma_j\beta_i)\sin(\Delta_{ij}\tau)$$

$$T_{I_{1x}\rightarrow I_{2z}I_{3y}} = \sum_{i=1}^{3} \gamma_i\alpha_i\sin(\Delta_{0i}\tau) - \sum_{i=1}^{3}\sum_{j=i+1}^{3} \nu_{ij}(\beta_i\alpha_j - \beta_j\alpha_i)\sin(\Delta_{ij}\tau)$$

$$T_{I_{1x}\rightarrow I_{3z}I_{2y}} = \sum_{i=1}^{3} \beta_i\alpha_i\sin(\Delta_{0i}\tau) - \sum_{i=1}^{3}\sum_{j=i+1}^{3} \nu_{ij}(\gamma_i\alpha_j - \gamma_j\alpha_i)\sin(\Delta_{ij}\tau)$$

$$T_{I_{1x}\rightarrow I_{1x}I_{2y}I_{3y}} = 2\sum_{i=1}^{3} \gamma_i\beta_i(\gamma_i^2 + \beta_i^2 - \alpha_i^2) + 2\sum_{i=1}^{3}\sum_{j=i+1}^{3} \nu_{ij}(\gamma_i\gamma_j + \beta_i\beta_j - \alpha_i\alpha_j)\cos(\Delta_{ij}\tau)$$

$$T_{I_{1x}\rightarrow I_{2x}I_{1y}I_{3y}} = 2\sum_{i=1}^{3} \gamma_i\beta_i(\gamma_i^2 - \beta_i^2 + \alpha_i^2) + 2\sum_{i=1}^{3}\sum_{j=i+1}^{3} \nu_{ij}(\gamma_i\gamma_j - \beta_i\beta_j + \alpha_i\alpha_j)\cos(\Delta_{ij}\tau)$$

$$T_{I_{1x}\rightarrow I_{3x}I_{1y}I_{2y}} = 2\sum_{i=1}^{3} \gamma_i\beta_i(-\gamma_i^2 + \beta_i^2 + \alpha_i^2) + 2\sum_{i=1}^{3}\sum_{j=i+1}^{3} \nu_{ij}(-\gamma_i\gamma_j + \beta_i\beta_j + \alpha_i\alpha_j)\cos(\Delta_{ij}\tau)$$

$$T_{I_{1x}\rightarrow I_{1x}I_{2x}I_{3z}} = -4\sum_{i=1}^{3} \gamma_i^2\beta_i^2 + 2\sum_{i=1}^{3} \alpha_i^2\cos(\Delta_{0i}\tau) - 2\sum_{i=1}^{3}\sum_{j=i+1}^{3} \nu_{ij}^2\cos(\Delta_{ij}\tau)$$

$$T_{I_{1x}\rightarrow I_{2x}I_{1z}I_{3z}} = -4\sum_{i=1}^{3} \gamma_i^2\beta_i\alpha_i + 2\sum_{i=1}^{3} \beta_i\alpha_i\cos(\Delta_{0i}\tau) - 2\sum_{i=1}^{3}\sum_{j=i+1}^{3} \nu_{ij}(\gamma_i\alpha_j + \gamma_j\alpha_i)\cos(\Delta_{ij}\tau)$$

$$T_{I_{1x}\rightarrow I_{3x}I_{1z}I_{2z}} = -4\sum_{i=1}^{3} \gamma_i\beta_i^2\alpha_i + 2\sum_{i=1}^{3} \gamma_i\alpha_i\cos(\Delta_{0i}\tau) - 2\sum_{i=1}^{3}\sum_{j=i+1}^{3} \nu_{ij}(\beta_i\alpha_j + \beta_j\alpha_i)\cos(\Delta_{ij}\tau)$$

Note. α_i, β_i, and γ_i are defined in Eq. [10] and $\nu_{ij} = (\alpha_i\beta_j + \alpha_j\beta_i)$.

maps where all planar scaling factors are held constant ($s_{kl}^{P} = 1$) whereas the (identical) longitudinal scaling factors ($s_{12}^{L} = s_{13}^{L} = s_{23}^{L}$) are varied between 5 and −5. This series includes the ideal cases of isotropic (Figs. 4E and 5E), planar (Figs. 4G and 5G), and dipolar (Figs. 4K and 5K) mixing for three coupled spins 1/2. If the coupling tensors are dominated by longitudinal coupling terms (cf. Figs. 4D, 4L, 5D, and 5L) the transfer of polarization and coherence between the spin pair 1–2 is effectively truncated except for some cases where the passive couplings J_{13} and J_{23} are approximately identical. Figures 4M–4O and 5M–5O correspond to the cases with (effective) planar coupling terms for spin pairs 1–3 and 2–3 where the coupling tensor for spin pair 1–2 is changed from isotropic (Figs. 4M and 5M) to dipolar (Figs. 4O and 5O) with an intermediate case shown in Figs. 4N and 5N. Corresponding maps are shown in Figs. 4P–4R and 5P–5R, except that here the coupling tensor for spin pair 1–3 is changed from isotropic (Figs. 4P and 5P) to dipolar (Figs. 4R and 5R) while planar

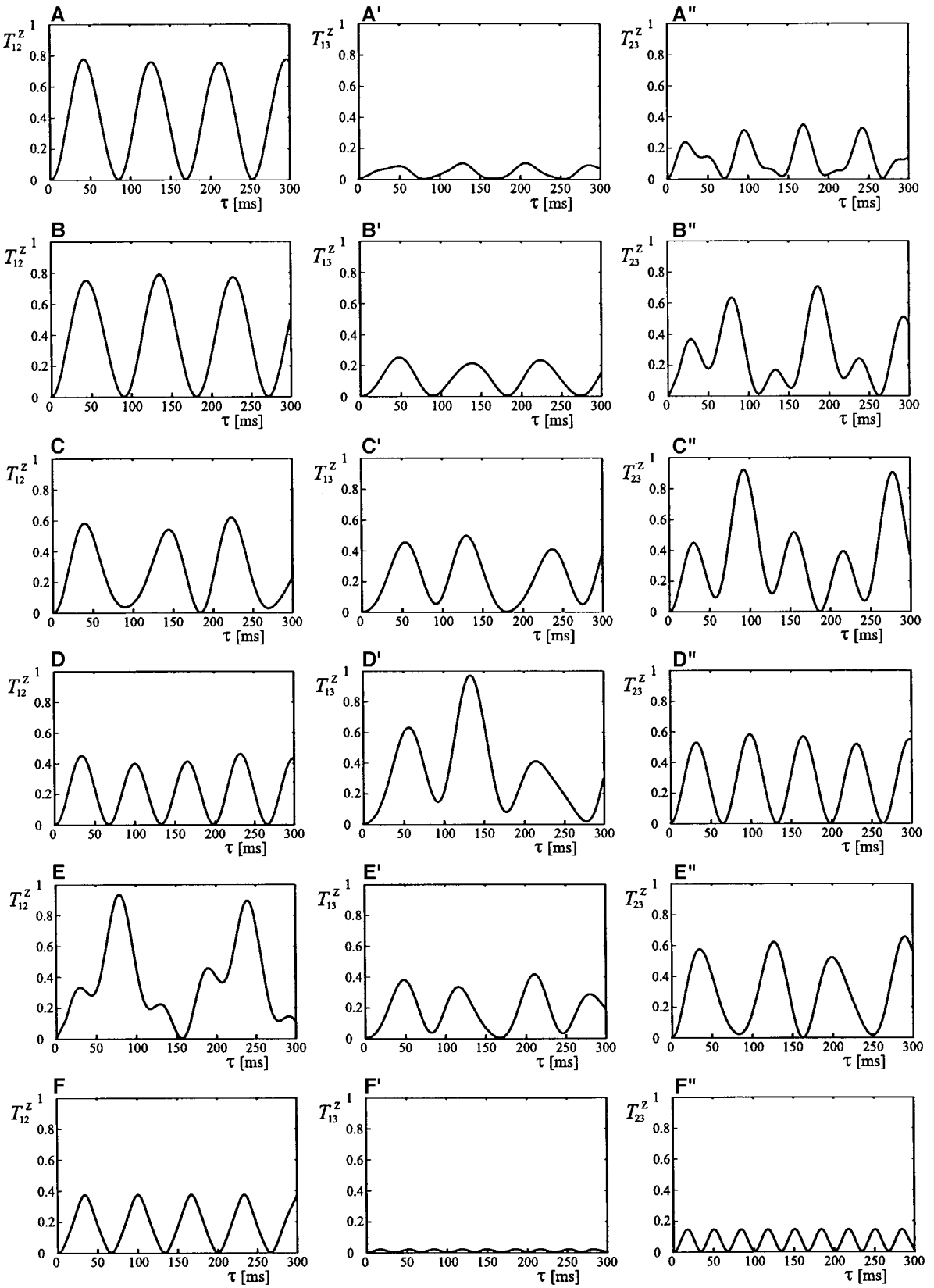

FIG. 2. Polarization transfer functions $T_{ij}^z = T_{I_{iz} \to I_{jz}}$ of a spin system consisting of three coupled spins 1/2 with $J_{12}^{\mathrm{P}} = -10$ Hz, $J_{13}^{\mathrm{P}} = 4.6$ Hz, and $J_{23}^{\mathrm{P}} = 11$ Hz under various cylindrical mixing conditions. (A–A″) $J_{ij}^{\mathrm{L}} = -2J_{ij}^{\mathrm{P}}$ (dipolar mixing, cf. (*35*)), (B–B″) $J_{ij}^{\mathrm{L}} = -J_{ij}^{\mathrm{P}}$, (C–C″) $J_{ij}^{\mathrm{L}} = -\frac{1}{2}J_{ij}^{\mathrm{P}}$, (D–D″) $J_{ij}^{\mathrm{L}} = 0$ (planar mixing, cf. (*19*)), (E–E″) $J_{ij}^{\mathrm{L}} = J_{ij}^{\mathrm{P}}$ (isotropic mixing, cf. (*34*)), and (F–F″) $J_{ij}^{\mathrm{L}} = 4J_{ij}^{\mathrm{P}}$.

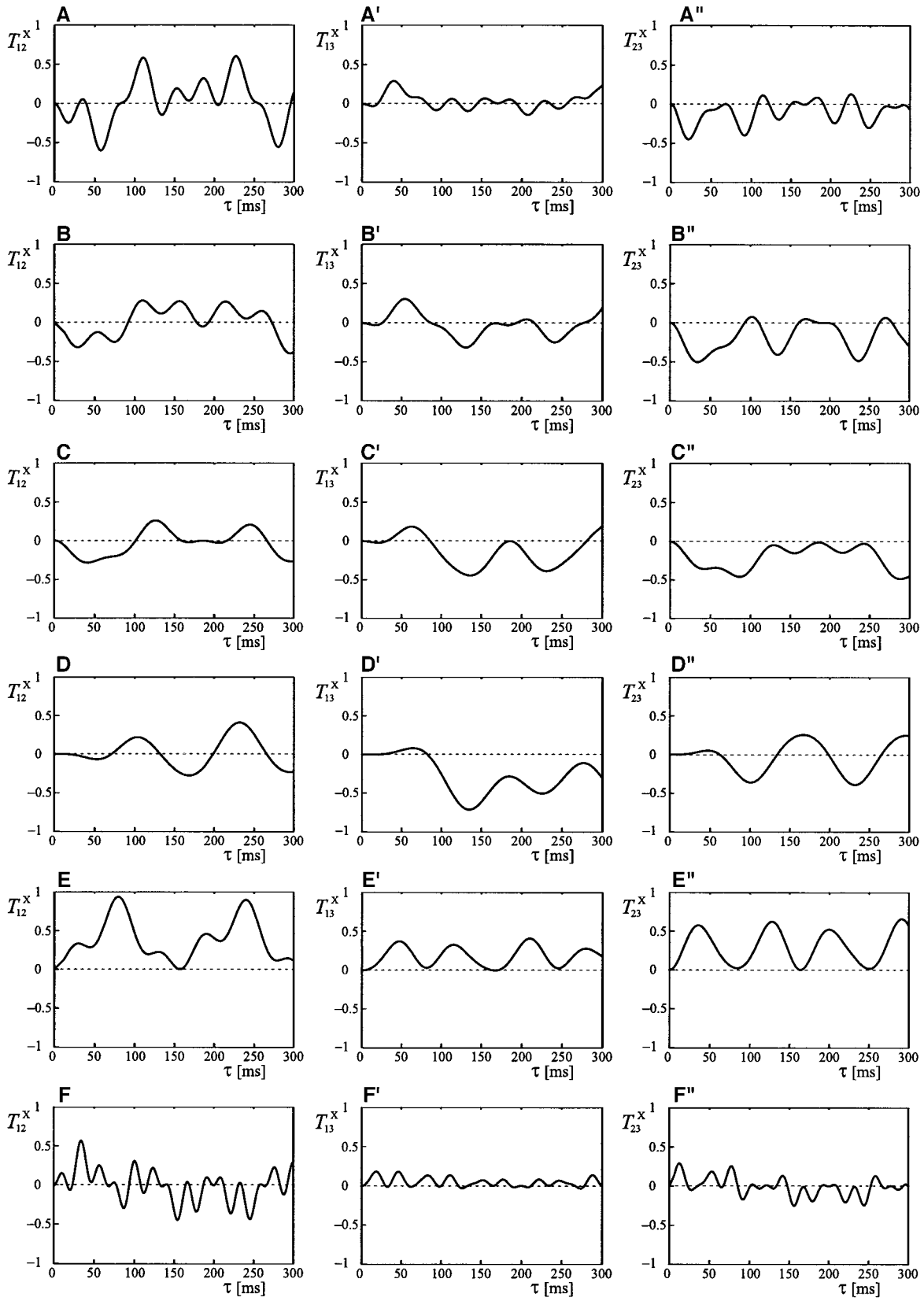

FIG. 3. Coherence transfer functions $T_{ij}^{x} = T_{I_{ix} \to I_{jx}}$ of a spin system consisting of three coupled spins 1/2 with $J_{12}^{P} = -10$ Hz, $J_{13}^{P} = 4.6$ Hz, and $J_{23}^{P} = 11$ Hz under various cylindrical mixing conditions. (A–A″) $J_{ij}^{L} = -2J_{ij}^{P}$ (dipolar mixing, cf. (*35*)), (B–B″) $J_{ij}^{L} = -J_{ij}^{P}$, (C–C″) $J_{ij}^{L} = -\frac{1}{2}J_{ij}^{P}$, (D–D″) $J_{ij}^{L} = 0$ (planar mixing), (E–E″) $J_{ij}^{L} = J_{ij}^{P}$ (isotropic mixing, cf. (*34*)), and (F–F″) $J_{ij}^{L} = 4J_{ij}^{P}$.

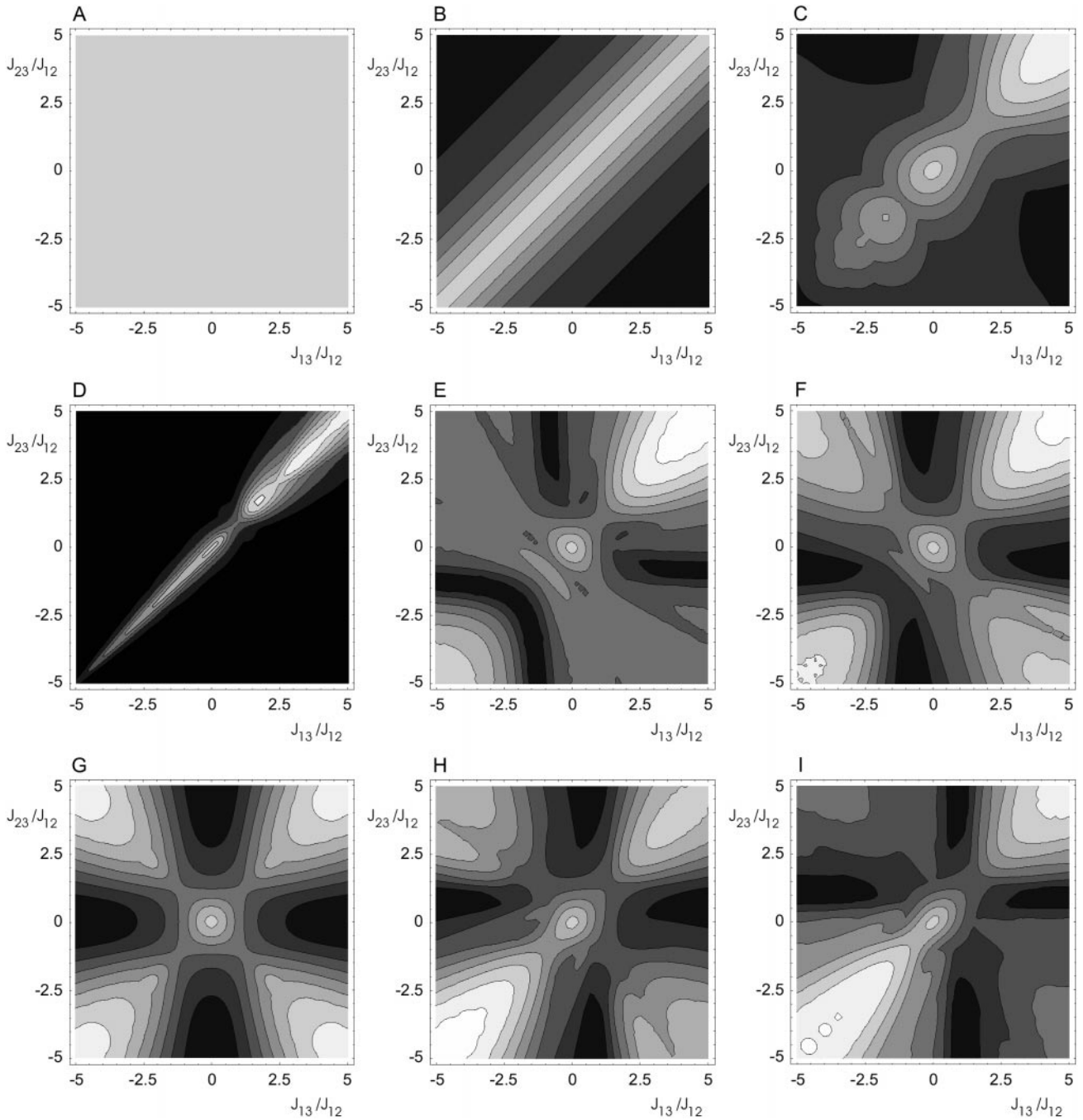

FIG. 4. Polarization transfer efficiency maps showing the quality factor η_{12}^{z} (Eq. [19]) as a function of the relative coupling constants J_{13}/J_{12} and J_{23}/J_{12} for a number of characteristic cases of cylindrical mixing defined by the set of planar and longitudinal scaling factors $\mathbf{s}^{P}$ and $\mathbf{s}^{L}$ (cf. Eq. [18]): (A) $\mathbf{s}^{P} = \{1, 0, 0\}$, $\mathbf{s}^{L} = \{1, 0, 0\}$ (corresponding to isotropic mixing for a two-spin system where $\eta_{12}^{z} = 0.62$ [10]), (B) $\mathbf{s}^{P} = \{1, 0, 0\}$, $\mathbf{s}^{L} = \{1, 1, 1\}$, (C) $\mathbf{s}^{P} = \{1, 0.5, 0.5\}$, $\mathbf{s}^{L} = \{1, 1, 1\}$. In (D)–(R) the planar scaling factors are $\mathbf{s}^{P} = \{1, 1, 1\}$ and the longitudinal scaling factors are (D) $\mathbf{s}^{L} = \{5, 5, 5\}$, (E) $\mathbf{s}^{L} = \{1, 1, 1\}$, (F) $\mathbf{s}^{L} = \{0.5, 0.5, 0.5\}$, (G) $\mathbf{s}^{L} = \{0, 0, 0\}$, (H) $\mathbf{s}^{L} = \{-0.5, -0.5, -0.5\}$, (I) $\mathbf{s}^{L} = \{-1, -1, -1\}$, (J) $\mathbf{s}^{L} = \{-1.5, -1.5, -1.5\}$, (K) $\mathbf{s}^{L} = \{-2, -2, -2\}$, (L) $\mathbf{s}^{L} = \{-5, -5, -5\}$, (M) $\mathbf{s}^{L} = \{1, 0, 0\}$, (N) $\mathbf{s}^{L} = \{-0.5, 0, 0\}$, (O) $\mathbf{s}^{L} = \{-2, 0, 0\}$, (P) $\mathbf{s}^{L} = \{0, 1, 0\}$, (Q) $\mathbf{s}^{L} = \{0, -0.5, 0\}$, (R) $\mathbf{s}^{L} = \{0, -2, 0\}$. The contour level increment is 0.1; in black areas $0 \leq \eta_{12}^{z} \leq 0.1$.

(effective) coupling terms exist for spin pairs 1–2 and 2–3. In practice, the maps shown in Figs. 4M–4O, 4P–4R, 5M–5O, and 5P–5R represent for example the case of heteronuclear planar mixing sequences, such as WALTZ-16 (*48*) or DIPSI-2 (*49*) applied to a spin system consisting of two homonuclear spins with an (effective) isotropic and/or dipolar coupling tensor and one additional heteronuclear spin. For such experiments, Figs. 4M–4O and 5M–5O reflect homonuclear whereas Figs. 4P–4R and 5P–5R reflect heteronuclear transfer efficiencies.

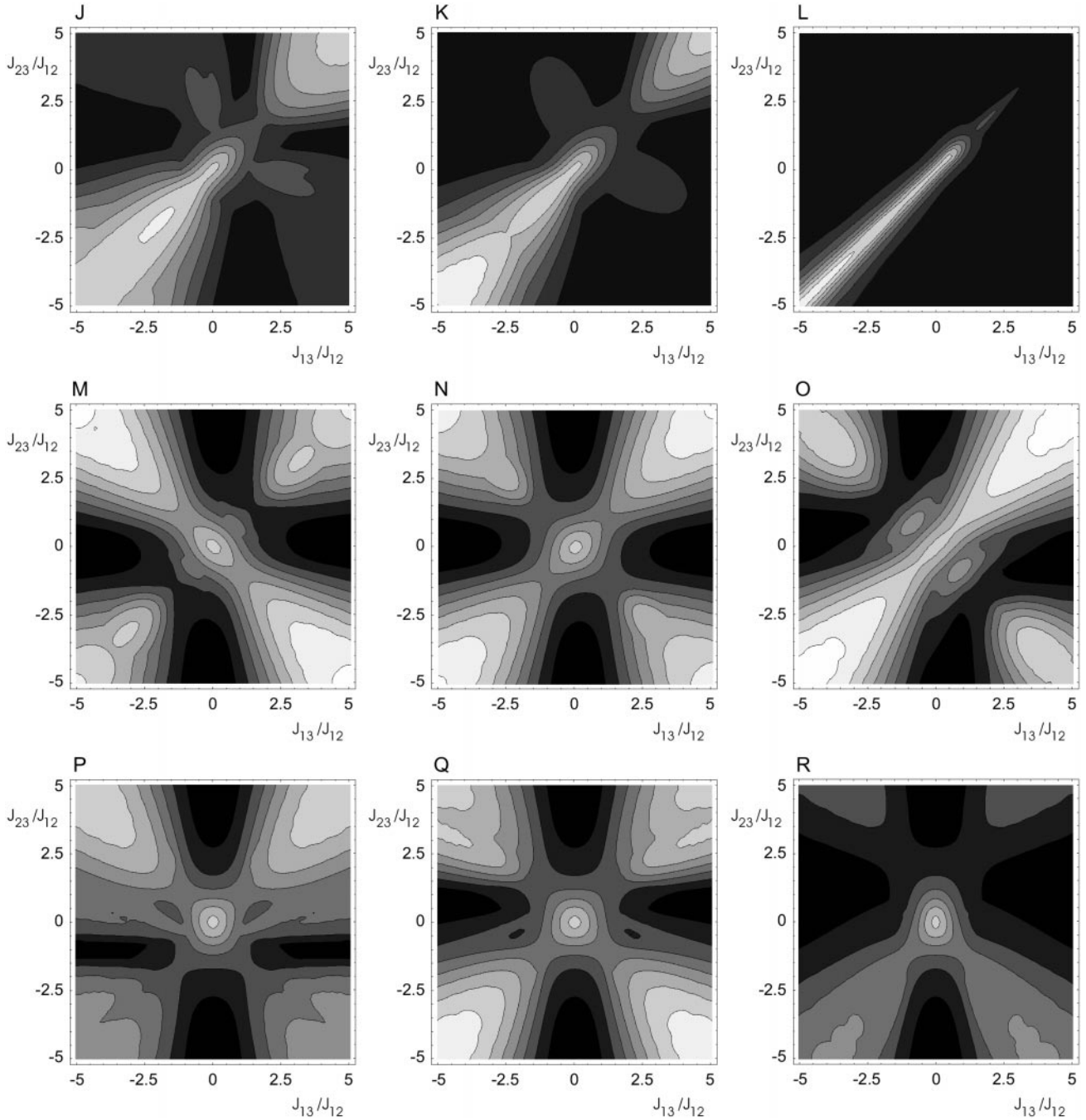

FIG. 4—*Continued*

CONCLUSION

For three spins 1/2, analytical polarization and coherence transfer functions were derived for general cylindrical mixing conditions, which result, e.g., from superpositions of scalar and (residual) dipolar coupling tensors. The general solutions include the special cases of dipolar, isotropic, planar, and longitudinal mixing. Whereas coherence transfer functions $T_{I_{kx}\rightarrow I_{lx}} = T_{I_{ky}\rightarrow I_{ly}}$ can also become negative (with the exception of isotropic mixing (*24*, *34*, *47*)), only positive polarization transfer functions $T_{I_{kz}\rightarrow I_{lz}}$ were found. Based on the quality factors η_{12}^{z} and η_{12}^{x} (Eq. [19]) transfer efficiency maps were shown in Figs. 4 and 5 for special cases of interest. However, the derived analytical transfer functions also apply to the general case of Hartmann–Hahn spectroscopy of partially oriented samples, where residual dipolar coupling constants are not correlated with the size of scalar couplings and hence arbitrary ratios $J_{ij}^{\mathrm{p}}/J_{ij}^{\mathrm{L}}$ are possible for each spin pair ij. In the

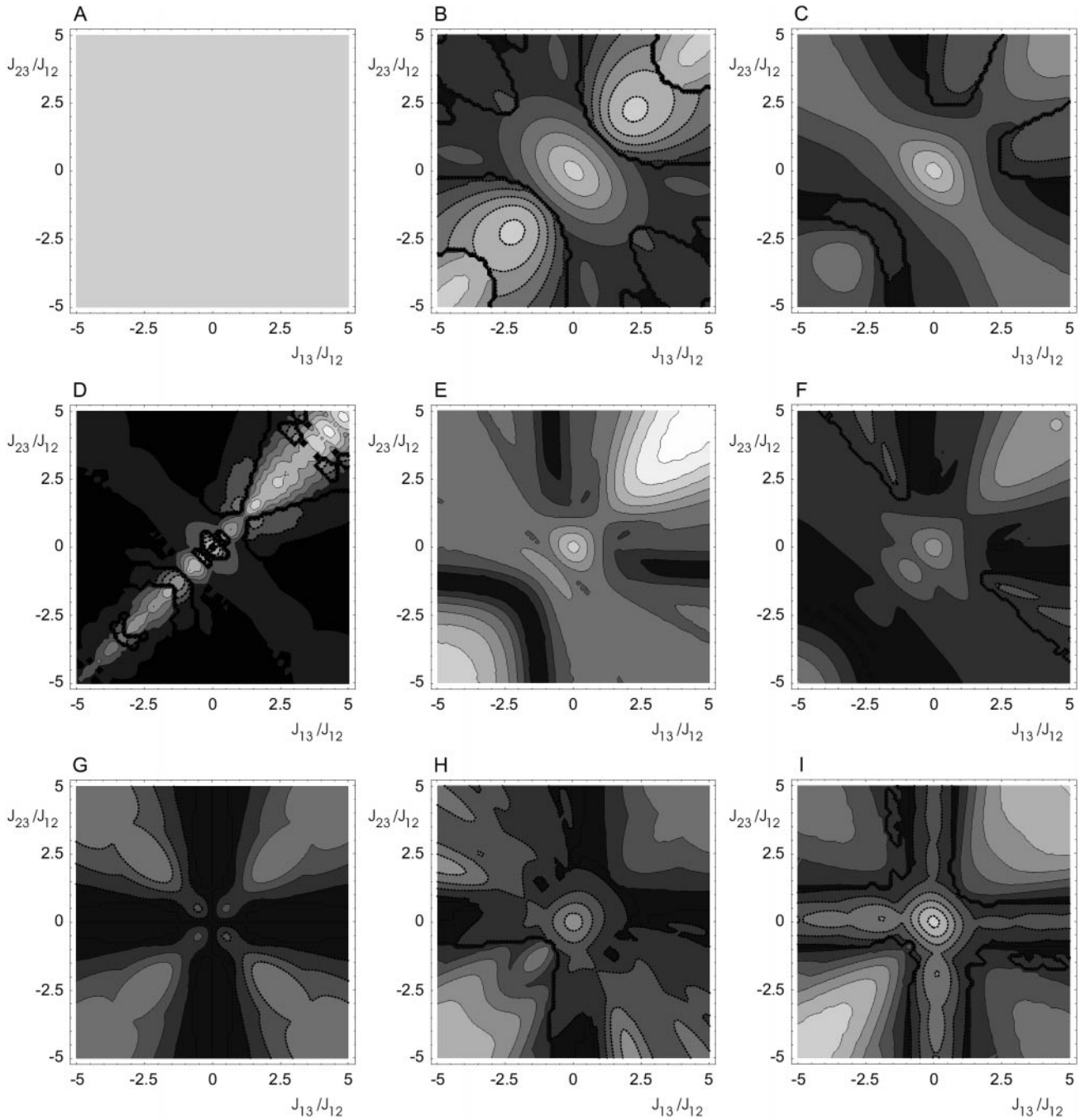

FIG. 5. Coherence transfer efficiency maps showing the quality factor $\eta_{12}^{x} = \eta_{12}^{y}$ (Eq. [19]) as a function of the relative coupling constants J_{13}/J_{12} and J_{23}/J_{12} for a number of characteristic cases of cylindrical mixing defined by the set of planar and longitudinal scaling factors $\mathbf{s}^{P}$ and $\mathbf{s}^{L}$ (cf. Eq. [18]): (A) $\mathbf{s}^{P} = \{1, 0, 0\}$, $\mathbf{s}^{L} = \{1, 0, 0\}$ (corresponding to isotropic mixing for a two-spin system where $\eta_{12}^{x} = 0.62$ [10]), (B) $\mathbf{s}^{P} = \{1, 0, 0\}$, $\mathbf{s}^{L} = \{1, 1, 1\}$, (C) $\mathbf{s}^{P} = \{1, 0.5, 0.5\}$, $\mathbf{s}^{L} = \{1, 1, 1\}$. In (D)–(R) the planar scaling factors are $\mathbf{s}^{P} = \{1, 1, 1\}$ and the longitudinal scaling factors are (D) $\mathbf{s}^{L} = \{5, 5, 5\}$, (E) $\mathbf{s}^{L} = \{1, 1, 1\}$, (F) $\mathbf{s}^{L} = \{0.5, 0.5, 0.5\}$, (G) $\mathbf{s}^{L} = \{0, 0, 0\}$, (H) $\mathbf{s}^{L} = \{-0.5, -0.5, -0.5\}$, (I) $\mathbf{s}^{L} = \{-1, -1, -1\}$, (J) $\mathbf{s}^{L} = \{-1.5, -1.5, -1.5\}$, (K) $\mathbf{s}^{L} = \{-2, -2, -2\}$, (L) $\mathbf{s}^{L} = \{-5, -5, -5\}$, (M) $\mathbf{s}^{L} = \{1, 0, 0\}$, (N) $\mathbf{s}^{L} = \{-0.5, 0, 0\}$, (O) $\mathbf{s}^{L} = \{-2, 0, 0\}$, (P) $\mathbf{s}^{L} = \{0, 1, 0\}$, (Q) $\mathbf{s}^{L} = \{0, -0.5, 0\}$, (R) $\mathbf{s}^{L} = \{0, -2, 0\}$. The contour level increment is 0.1; in black areas $|\eta_{12}^{x}| = |\eta_{12}^{y}| \leq 0.1$. Negative levels are indicated by dashed contour lines.

mixing period of homonuclear Hartmann–Hahn experiments applied to samples with residual dipolar couplings (*23*), WALTZ-16 (*48*) and DIPSI-2 (*49*) sequences can be used to create energy matched conditions. Similar to cw_x irradiation, these sequences create effective coupling terms that have the form of Eq. [1] if the axis labels $\{x, y, z\}$ are replaced by $\{y, z, x\}$ and with a reduced effective dipolar coupling constant $D_{\text{eff}} = -D/2$ (*50*). Hence, the analytical transfer functions summarized in Tables 1, 2, and 3 are also valid for these mixing sequences if the axis labels are permuted and if in Eq.

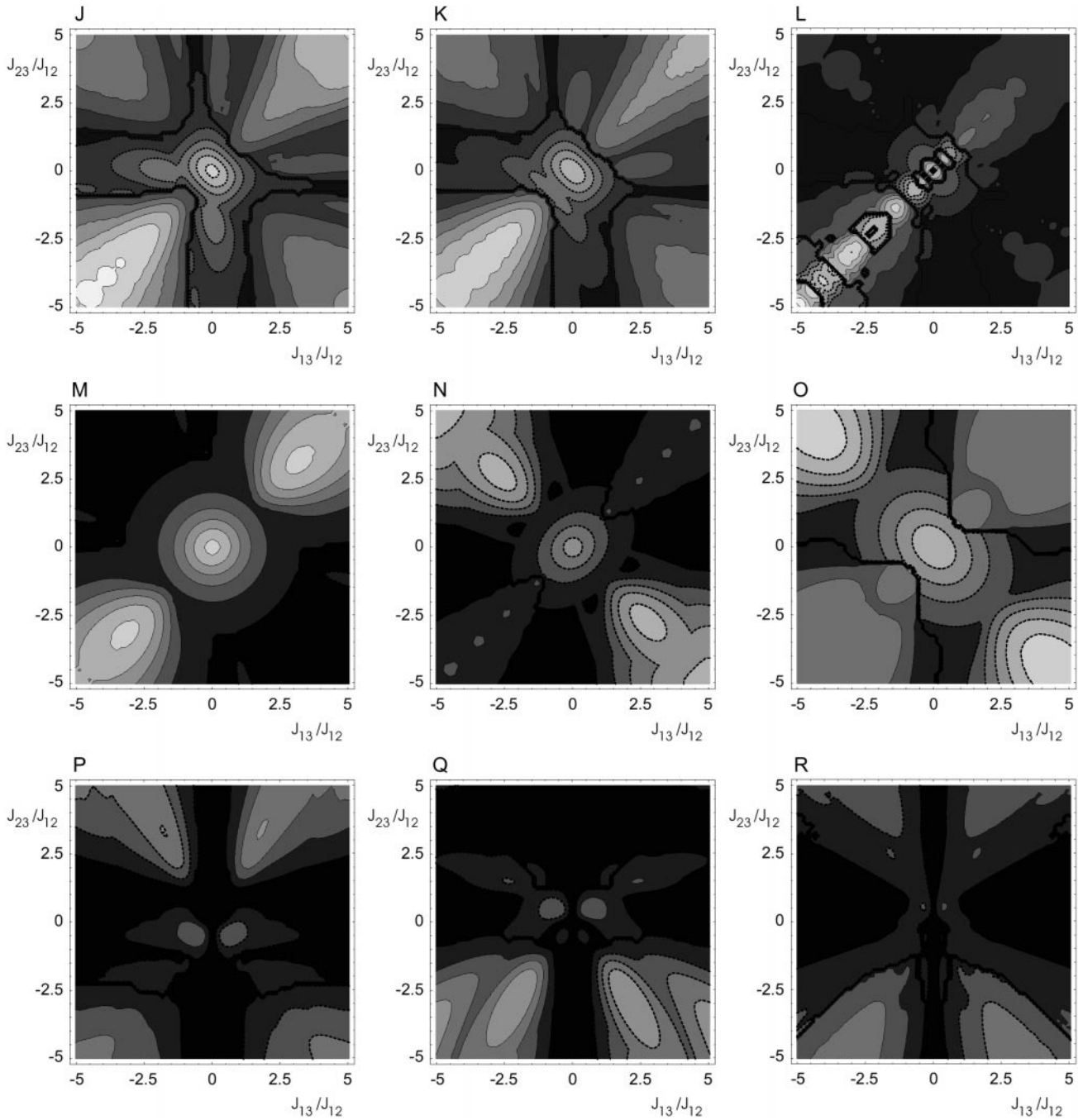

FIG. 5—*Continued*

[2] the dipolar coupling constants are replaced by the scaled effective dipolar coupling constants D_{eff}. It should also be kept in mind that for a given multiple-pulse sequence the form of the effective coupling tensors depends in general also on the offsets of the coupled spins (*32*). The derived transfer functions form a theoretical basis to understand the transfer dynamics under cylindrical mixing conditions, which are created, for example, in Hartmann–Hahn experiments in the presence of residual dipolar couplings.

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