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Response of a coupled two-spin system to on-resonance amplitude modulated RF pulses

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A weakly scalar-coupled two-spin system subjected to two amplitude modulated RF pulses on exact resonance is treated by means of the rotation operator approach. The theory presented here enables coherence evolution to be evaluated by the routine procedure and to be expressed in analytical form. The evolution behaviour from the equilibrium state is discussed in some detail. It is shown that the application of rotation matrix and quaternion elements clarifies evolution expressions. The numerical calculation is performed by way of quaternions. Examples of BURP (band-selective, uniform response, pure-phase) and sinc-shaped RF pulses are given and the case of time-symmetrical RF pulses is analysed further.

1. Introduction

The response of a coupled spin system to shaped RF pulses is of practical importance since spins may always couple together somehow. One interesting case is when a shaped RF pulse affects only a single spin or group of magnetically equivalent spins in a scalar-coupled spin system [1]. It was shown [2] that such a case can be described adequately by means of the rotation operator approach [3]. In the present paper, the important case is taken into account where both spins in a scalar-coupled two-spin system are excited simultaneously by two on-resonance amplitude modulated RF pulses [4–8]. Blechta and Schraml have already put forward a novel analytical description for this case [7], but as can be seen later, not only is our theory formally more straightforward, but also it retains many of the advantages of the widely accepted density operator formalism [9–12].

2. The Hamiltonian and propagator

Consider a weakly scalar-coupled two-spin system (I and S, both spin-1/2) which are irradiated by on-resonance amplitude modulated RF pulses applied along the x axis. In the usual doubly rotating frame, the spin Hamiltonian can be written as

$$\mathscr{H}(t) = \omega_{1I}(t) I_x + \omega_{1S}(t) S_x + 2\pi J I_z S_z, \tag{1}$$

where ω_{1I} and ω_{1S} are two RF field strengths, and $2\pi J$ denotes the scalar-coupling

Table 1. The transformations of product operators from the doubly rotating frame into the doubly rotating tilted frame defined by equation (2).

$I_x \to -2I_x S_x$;	$I_y \to I_y$;	$I_z \to -2I_z S_x$
$S_x \to 2I_y S_y$;	$S_y \to -2I_y S_z$;	$S_z \to -S_x$
$2I_x S_x \to 2I_z S_z$;	$2I_x S_y \to 2I_z S_y$;	$2I_x S_z \to I_x$
$2I_y S_x \to S_y$;	$2I_y S_y \to -S_z$;	$2I_y S_z \to -2I_y S_x$
$2I_z S_x \to -2I_x S_z$;	$2I_z S_y \to -2I_x S_y$;	$2I_z S_z \to I_z$

Table 2. The relationship between product operators and single-transition operators for a two-spin-1/2 system.

First subset	$I_x = I_x^{13} + I_x^{24}$;	$S_x = I_x^{12} + I_x^{34}$
	$I_y = I_y^{13} + I_y^{24}$;	$S_y = I_y^{12} + I_y^{34}$
	$2I_x S_z = I_x^{13} - I_x^{24}$;	$2I_z S_x = I_x^{12} - I_x^{34}$
	$2I_y S_z = I_y^{13} - I_y^{24}$;	$2I_z S_y = I_y^{12} - I_y^{34}$
Second subset	$2I_x S_x = I_x^{14} + I_x^{23}$;	$2I_x S_y = I_y^{14} - I_y^{23}$
	$2I_y S_x = I_y^{14} + I_y^{23}$;	$2I_y S_y = -I_x^{14} + I_x^{23}$
Third subset[a]	$I_z = I_z^{14} + I_z^{23}$;	$S_z = I_z^{14} - I_z^{23}$
	$2I_z S_z = \frac{1}{2}(\mathbf{1}^{14} - \mathbf{1}^{23})$	

[a] Here $\mathbf{1}^{14}$ and $\mathbf{1}^{23}$ are two unit operators.

coefficient. This form of the spin Hamiltonian, different from our previous definition [2, 3], is similar to that in some relevant articles [4, 7, 8], which corresponds to such a rotation $I_z \to -I_y \to -I_z \to I_y$. Furthermore, a tilted frame (T) can be introduced,

$$\rho^{\mathrm{T}} = \exp(i\pi I_y S_x) \exp[i\tfrac{\pi}{2}(I_y + S_y)] \rho \exp[-i\tfrac{\pi}{2}(I_y + S_y)] \exp(-i\pi I_y S_x). \qquad (2)$$

Table 1 lists the transformations of product operators from the doubly rotating frame into the doubly rotating tilted frame. Equation (1) can thus be recast into the form

$$\mathscr{H}^{\mathrm{T}}(t) = -\omega_{1\mathrm{I}}(t)\, 2I_x S_x + \omega_{1\mathrm{S}}(t)\, 2I_y S_y + \pi J I_z. \qquad (3)$$

There are several different but related base operators that can be selected for the expansion of the density operator and the spin Hamiltonian. For convenience, the relationships between product operators [9, 10] and single-transition operators [11] (or fictitious spin-1/2 operators [12]) are listed in table 2. By employing the single-transition operator formalism, the Hamiltonian $\mathscr{H}^{\mathrm{T}}(t)$ can be expressed as

$$\mathscr{H}^{\mathrm{T}}(t) = \mathscr{H}^{\Sigma}(t) + \mathscr{H}^{\Delta}(t), \qquad (4)$$

with

$$\mathscr{H}^{\Sigma}(t) = -\omega_{\Sigma}(t)\, I_x^{14} + \pi J I_z^{14}, \qquad (5a)$$

$$\mathscr{H}^{\Delta}(t) = -\omega_{\Delta}(t)\, I_x^{23} + \pi J I_z^{23}, \qquad (5b)$$

where $\omega_{\Sigma}(t) = \omega_{1\mathrm{I}}(t) + \omega_{1\mathrm{S}}(t)$ and $\omega_{\Delta}(t) = \omega_{1\mathrm{I}}(t) - \omega_{1\mathrm{S}}(t)$. This construction has the advantage that the two parts $\mathscr{H}^{\Sigma}$ and $\mathscr{H}^{\Delta}$ commute at all times. They can be referred to as the double-quantum (DQ) and zero-quantum (ZQ) parts of the spin Hamiltonian, characterized by the sum and difference of the strengths of two shaped RF pulses, $\omega_{1\mathrm{I}}(t)$ and $\omega_{1\mathrm{S}}(t)$, respectively. Therefore, the propagator can also be divided into two commuting parts,

$$U^{\mathrm{T}}(t) = U^{\Sigma}(t)\, U^{\Delta}(t). \qquad (6)$$

As explained in [3], the propagators $U^{\Delta}(t)$ and $U^{\Sigma}(t)$ can be disentangled into the form of a rotation operator. For example,

$$U^{\Delta}(t) = \exp[i\gamma_{\Delta}(t)\, I_z^{23}]\exp[i\beta_{\Delta}(t)\, I_y^{23}]\exp[i\alpha_{\Delta}(t)\, I_z^{23}], \tag{7}$$

where the three time-dependent Euler angles $(\alpha_{\Delta}(t), \beta_{\Delta}(t), \gamma_{\Delta}(t))$ satisfy the Euler geometric equations [3]

$$\dot{\gamma}_{\Delta} + \dot{\alpha}_{\Delta}\cos\beta_{\Delta} = -\pi J, \tag{8a}$$

$$\dot{\beta}_{\Delta} = \omega_{\Delta}(t)\sin\gamma_{\Delta}, \tag{8b}$$

$$\dot{\alpha}_{\Delta}\sin\beta_{\Delta} = -\omega_{\Delta}(t)\cos\gamma_{\Delta}, \tag{8c}$$

with the initial conditions $\alpha_{\Delta}(0) = -\pi/2$, $\beta_{\Delta}(0) = 0$, and $\gamma_{\Delta}(0) = \pi/2$. We have presented already analytical and numerical solutions of these three characteristic equations [3]. Those solutions can of course be applied to treat the present problem.

3. Evolution of coherence

Since the propagator $U^{\mathrm{T}}(t)$ has been disentangled into a cascade of simple exponential operators which obviates the Dyson time-ordering operator, the evolution of the density operator under the influence of $\mathscr{H}^{\mathrm{T}}(t)$ can be evaluated by the standard procedure [9–12]. On the one hand, we can derive readily two independent evolution expressions as follows:

$$\begin{bmatrix} I_x^{23} \\ I_y^{23} \\ I_z^{23} \end{bmatrix} \xrightarrow{U^{\Delta}} R(\alpha_{\Delta}, \beta_{\Delta}, \gamma_{\Delta}) \begin{bmatrix} I_x^{23} \\ I_y^{23} \\ I_z^{23} \end{bmatrix}, \tag{9a}$$

$$\begin{bmatrix} I_x^{14} \\ I_y^{14} \\ I_z^{14} \end{bmatrix} \xrightarrow{U^{\Sigma}} R(\alpha_{\Sigma}, \beta_{\Sigma}, \gamma_{\Sigma}) \begin{bmatrix} I_x^{14} \\ I_y^{14} \\ I_z^{14} \end{bmatrix}, \tag{9b}$$

where two coefficient matrices specifying the evolution of the coherence are of the form of a rotation matrix in a three-dimensional space

$$R(\alpha, \beta, \gamma) = \begin{bmatrix} -\sin\alpha\sin\gamma + \cos\alpha\cos\beta\cos\gamma & -\sin\alpha\cos\gamma - \cos\alpha\cos\beta\sin\gamma & \cos\alpha\sin\beta \\ \cos\alpha\sin\gamma + \sin\alpha\cos\beta\sin\gamma & \cos\alpha\cos\gamma - \sin\alpha\cos\beta\sin\gamma & \sin\alpha\sin\beta \\ -\sin\beta\cos\gamma & \sin\beta\sin\gamma & \cos\beta \end{bmatrix}. \tag{10}$$

According to table 2, combinations of equations (9*a*, *b*) can be used to evaluate the evolution expressions for the product operators $2I_x S_x$, $2I_x S_y$, $2I_y S_x$, $2I_y S_y$, I_z, and S_z under the action of $\mathscr{H}^{\mathrm{T}}(t)$, i.e., in the doubly rotating tilted frame. By using equation (2) or table 1, these expressions can be transformed back readily into those of the product operators I_x, S_x, $2I_y S_z$, $2I_z S_y$, $2I_y S_y$, and $2I_z S_z$ under the influence of $\mathscr{H}(t)$, i.e., in the doubly rotating frame, and the results are listed in table 3.

Table 3. The evolution of product operators under the influence of $\mathscr{H}(t)$ using rotation matrix elements.

$$I_x \xrightarrow{U} \tfrac{1}{2}(R^{\Sigma}_{11}+R^{\Delta}_{11})\,I_x+\tfrac{1}{2}(R^{\Sigma}_{11}-R^{\Delta}_{11})\,S_x+\tfrac{1}{2}(R^{\Sigma}_{12}+R^{\Delta}_{12})\,2I_yS_z$$
$$+\tfrac{1}{2}(R^{\Sigma}_{12}-R^{\Delta}_{12})\,2I_zS_y+\tfrac{1}{2}(R^{\Sigma}_{13}-R^{\Delta}_{13})\,2I_yS_y-\tfrac{1}{2}(R^{\Sigma}_{13}+R^{\Delta}_{13})\,2I_zS_z$$

$$S_x \xrightarrow{U} \tfrac{1}{2}(R^{\Sigma}_{11}-R^{\Delta}_{11})\,I_x+\tfrac{1}{2}(R^{\Sigma}_{11}+R^{\Delta}_{11})\,S_x+\tfrac{1}{2}(R^{\Sigma}_{12}-R^{\Delta}_{12})\,2I_yS_z$$
$$+\tfrac{1}{2}(R^{\Sigma}_{12}+R^{\Delta}_{12})\,2I_zS_y+\tfrac{1}{2}(R^{\Sigma}_{13}+R^{\Delta}_{13})\,2I_yS_y-\tfrac{1}{2}(R^{\Sigma}_{13}-R^{\Delta}_{13})\,2I_zS_z$$

$$2I_yS_z \xrightarrow{U} \tfrac{1}{2}(R^{\Sigma}_{21}+R^{\Delta}_{21})\,I_x+\tfrac{1}{2}(R^{\Sigma}_{21}-R^{\Delta}_{21})\,S_x+\tfrac{1}{2}(R^{\Sigma}_{22}+R^{\Delta}_{22})\,2I_yS_z$$
$$+\tfrac{1}{2}(R^{\Sigma}_{22}-R^{\Delta}_{22})\,2I_zS_y+\tfrac{1}{2}(R^{\Sigma}_{23}-R^{\Delta}_{23})\,2I_yS_y-\tfrac{1}{2}(R^{\Sigma}_{23}+R^{\Delta}_{23})\,2I_zS_z$$

$$2I_zS_y \xrightarrow{U} \tfrac{1}{2}(R^{\Sigma}_{21}-R^{\Delta}_{21})\,I_x+\tfrac{1}{2}(R^{\Sigma}_{21}+R^{\Delta}_{21})\,S_x+\tfrac{1}{2}(R^{\Sigma}_{22}-R^{\Delta}_{22})\,2I_yS_z$$
$$+\tfrac{1}{2}(R^{\Sigma}_{22}+R^{\Delta}_{22})\,2I_zS_y+\tfrac{1}{2}(R^{\Sigma}_{23}+R^{\Delta}_{23})\,2I_yS_y-\tfrac{1}{2}(R^{\Sigma}_{23}-R^{\Delta}_{23})\,2I_zS_z$$

$$2I_yS_y \xrightarrow{U} \tfrac{1}{2}(R^{\Sigma}_{31}-R^{\Delta}_{31})\,I_x+\tfrac{1}{2}(R^{\Sigma}_{31}+R^{\Delta}_{31})\,S_x+\tfrac{1}{2}(R^{\Sigma}_{32}-R^{\Delta}_{32})\,2I_yS_z$$
$$+\tfrac{1}{2}(R^{\Sigma}_{32}+R^{\Delta}_{32})\,2I_zS_y+\tfrac{1}{2}(R^{\Sigma}_{33}+R^{\Delta}_{33})\,2I_yS_y-\tfrac{1}{2}(R^{\Sigma}_{33}-R^{\Delta}_{33})\,2I_zS_z$$

$$2I_zS_z \xrightarrow{U} -\tfrac{1}{2}(R^{\Sigma}_{31}+R^{\Delta}_{31})\,I_x-\tfrac{1}{2}(R^{\Sigma}_{31}-R^{\Delta}_{31})\,S_x-\tfrac{1}{2}(R^{\Sigma}_{32}+R^{\Delta}_{32})\,2I_yS_z$$
$$-\tfrac{1}{2}(R^{\Sigma}_{32}-R^{\Delta}_{32})\,2I_zS_y-\tfrac{1}{2}(R^{\Sigma}_{33}-R^{\Delta}_{33})\,2I_yS_y+\tfrac{1}{2}(R^{\Sigma}_{33}+R^{\Delta}_{33})\,2I_zS_z$$

Table 4. The evolution of product operators under the action of $\mathscr{H}(t)$ using quaternion elements.

$$I_y \xrightarrow{U} -(c_\Delta c_\Sigma-d_\Delta d_\Sigma+a_\Delta a_\Sigma-b_\Delta b_\Sigma)\,I_y-(c_\Delta b_\Sigma-d_\Delta a_\Sigma-a_\Delta d_\Sigma+b_\Delta c_\Sigma)\,I_z$$
$$-(c_\Delta a_\Sigma+d_\Delta b_\Sigma-a_\Delta c_\Sigma-b_\Delta d_\Sigma)\,2I_xS_y+(c_\Delta d_\Sigma+d_\Delta c_\Sigma+a_\Delta b_\Sigma+b_\Delta a_\Sigma)\,2I_xS_z$$

$$I_z \xrightarrow{U} -(c_\Delta b_\Sigma+d_\Delta a_\Sigma+a_\Delta d_\Sigma+b_\Delta c_\Sigma)\,I_y+(c_\Delta c_\Sigma+d_\Delta d_\Sigma-a_\Delta a_\Sigma-b_\Delta b_\Sigma)\,I_z$$
$$-(c_\Delta d_\Sigma-d_\Delta c_\Sigma-a_\Delta b_\Sigma+b_\Delta a_\Sigma)\,2I_xS_y-(c_\Delta a_\Sigma-d_\Delta b_\Sigma+a_\Delta c_\Sigma-b_\Delta d_\Sigma)\,2I_xS_z$$

$$2I_xS_y \xrightarrow{U} -(c_\Delta a_\Sigma-d_\Delta b_\Sigma-a_\Delta c_\Sigma+b_\Delta d_\Sigma)\,I_y+(c_\Delta d_\Sigma-d_\Delta c_\Sigma+a_\Delta b_\Sigma-b_\Delta a_\Sigma)\,I_z$$
$$+(c_\Delta c_\Sigma+d_\Delta d_\Sigma+a_\Delta a_\Sigma+b_\Delta b_\Sigma)\,2I_xS_y+(c_\Delta b_\Sigma+d_\Delta a_\Sigma-a_\Delta d_\Sigma-b_\Delta c_\Sigma)\,2I_xS_z$$

$$2I_xS_z \xrightarrow{U} -(c_\Delta d_\Sigma+d_\Delta c_\Sigma-a_\Delta b_\Sigma-b_\Delta a_\Sigma)\,I_y-(c_\Delta a_\Sigma+d_\Delta b_\Sigma+a_\Delta c_\Sigma+b_\Delta d_\Sigma)\,I_z$$
$$+(c_\Delta b_\Sigma-d_\Delta a_\Sigma+a_\Delta d_\Sigma-b_\Delta c_\Sigma)\,2I_xS_y-(c_\Delta c_\Sigma-d_\Delta d_\Sigma-a_\Delta a_\Sigma+b_\Delta b_\Sigma)\,2I_xS_z$$

$$S_y \xrightarrow{U} -(c_\Delta c_\Sigma-d_\Delta d_\Sigma-a_\Delta a_\Sigma+b_\Delta b_\Sigma)\,S_y-(c_\Delta b_\Sigma-d_\Delta a_\Sigma+a_\Delta d_\Sigma-b_\Delta c_\Sigma)\,S_z$$
$$+(c_\Delta a_\Sigma+d_\Delta b_\Sigma+a_\Delta c_\Sigma+b_\Delta d_\Sigma)\,2I_yS_x+(c_\Delta d_\Sigma+d_\Delta c_\Sigma-a_\Delta b_\Sigma-b_\Delta a_\Sigma)\,2I_zS_x$$

$$S_z \xrightarrow{U} -(c_\Delta b_\Sigma+d_\Delta a_\Sigma-a_\Delta d_\Sigma-b_\Delta c_\Sigma)\,S_y+(c_\Delta c_\Sigma+d_\Delta d_\Sigma+a_\Delta a_\Sigma+b_\Delta b_\Sigma)\,S_z$$
$$-(c_\Delta d_\Sigma-d_\Delta c_\Sigma+a_\Delta b_\Sigma-b_\Delta a_\Sigma)\,2I_yS_x-(c_\Delta a_\Sigma-d_\Delta b_\Sigma-a_\Delta c_\Sigma+b_\Delta d_\Sigma)\,2I_zS_x$$

$$2I_yS_x \xrightarrow{U} -(c_\Delta a_\Sigma-d_\Delta b_\Sigma+a_\Delta c_\Sigma-b_\Delta d_\Sigma)\,S_y+(c_\Delta d_\Sigma-d_\Delta c_\Sigma-a_\Delta b_\Sigma+b_\Delta a_\Sigma)\,S_z$$
$$+(c_\Delta c_\Sigma+d_\Delta d_\Sigma-a_\Delta a_\Sigma-b_\Delta b_\Sigma)\,2I_yS_x+(c_\Delta b_\Sigma+d_\Delta a_\Sigma+a_\Delta b_\Sigma+b_\Delta c_\Sigma)\,2I_zS_x$$

$$2I_zS_x \xrightarrow{U} -(c_\Delta d_\Sigma+d_\Delta c_\Sigma+a_\Delta b_\Sigma+b_\Delta a_\Sigma)\,S_y-(c_\Delta a_\Sigma+b_\Delta d_\Sigma-a_\Delta c_\Sigma-b_\Delta d_\Sigma)\,S_z$$
$$+(c_\Delta b_\Sigma-d_\Delta a_\Sigma+a_\Delta b_\Sigma-b_\Delta c_\Sigma)\,2I_yS_x-(c_\Delta c_\Sigma-d_\Delta d_\Sigma+a_\Delta a_\Sigma-b_\Delta b_\Sigma)\,2I_zS_x$$

On the other hand, the problem can be solved by the use of quaternions. As shown previously [2], we have

$$\begin{bmatrix} I_x \\ I_y \\ 2I_z S_x \\ 2I_z S_y \end{bmatrix} \xrightarrow{U^\Delta} M(a_\Delta, b_\Delta, c_\Delta, d_\Delta) \begin{bmatrix} I_x \\ I_y \\ 2I_z S_x \\ 2I_z S_y \end{bmatrix}, \tag{11a}$$

$$\begin{bmatrix} S_x \\ S_y \\ 2I_x S_z \\ 2I_y S_z \end{bmatrix} \xrightarrow{U^\Delta} N(a_\Delta, b_\Delta, c_\Delta, d_\Delta) \begin{bmatrix} S_x \\ S_y \\ 2I_x S_z \\ 2I_y S_z \end{bmatrix}, \tag{11b}$$

$$\begin{bmatrix} I_x \\ I_y \\ 2I_z S_x \\ 2I_z S_y \end{bmatrix} \xrightarrow{U^\Sigma} O(a_\Sigma, b_\Sigma, c_\Sigma, d_\Sigma) \begin{bmatrix} I_x \\ I_y \\ 2I_z S_x \\ 2I_z S_y \end{bmatrix}, \tag{11c}$$

$$\begin{bmatrix} S_x \\ S_y \\ 2I_x S_z \\ 2I_y S_z \end{bmatrix} \xrightarrow{U^\Sigma} O(a_\Sigma, b_\Sigma, c_\Sigma, d_\Sigma) \begin{bmatrix} S_x \\ S_y \\ 2I_x S_z \\ 2I_y S_z \end{bmatrix}, \tag{11d}$$

with

$$M(a,b,c,d) = \begin{bmatrix} d & -c & b & a \\ c & d & -a & b \\ -b & a & d & c \\ -a & -b & -c & d \end{bmatrix}, \quad N(a,b,c,d) = \begin{bmatrix} d & c & -b & a \\ -c & d & -a & -b \\ b & a & d & -c \\ -a & b & c & d \end{bmatrix},$$

$$O(a,b,c,d) = \begin{bmatrix} d & -c & b & -a \\ c & d & -a & -b \\ -b & a & d & -c \\ a & b & c & d \end{bmatrix}, \tag{12}$$

where the four coefficients (a, b, c, d) are known as quaternion elements [13–15] which describe a rotation in a three-dimensional space and which are defined by

$$a = \sin\frac{\gamma-\alpha}{2}\sin\frac{\beta}{2}, \quad b = \cos\frac{\gamma-\alpha}{2}\sin\frac{\beta}{2}, \quad c = \sin\frac{\gamma+\alpha}{2}\cos\frac{\beta}{2}, \quad d = \cos\frac{\gamma+\alpha}{2}\cos\frac{\beta}{2}, \tag{13}$$

obeying the relation $a^2+b^2+c^2+d^2 = 1$. The evolution expressions for the product operators I_y, I_z, $2I_x S_y$, and $2I_x S_z$ caused by $\mathscr{H}(t)$ can thus be obtained by the use of equations (11 *a*, *c*) along with table 1. Similarly, those of product operators S_y, S_z, $2I_y S_x$, and $2I_z S_x$ due to $\mathscr{H}(t)$ can be obtained also. Table 4 summarizes the evolution expressions of these product operators. More importantly, the evolution of the coherence can be characterized in terms of the quaternion elements of the corresponding rotation operators.

It is worthwhile pointing out that by defining a phase-shifted tilted frame (T′), the aforementioned formulation can be applied to the case of two RF pulses in an arbitrary direction. For example, for the case of both RF fields along the y axis (phase shift $\pi/2$), we may define

$$\rho^{\mathrm{T}'} = \exp(i\pi I_y S_x)\exp[i\tfrac{\pi}{2}(I_y+S_y)]\exp[i\tfrac{\pi}{2}(I_z+S_z)]\rho\exp[-i\tfrac{\pi}{2}(I_z+S_z)] \exp[-i\tfrac{\pi}{2}(I_y+S_y)]\exp(-i\pi I_y S_x). \quad (14)$$

Comparing this with equation (2) for two RF pulses along the x axis, it is clear that corresponding to every phase-shifted tilted frame we simply have some different transformations between product operators.

Two special cases are now discussed in some detail. One is when only a single spin (spin I, say) in a coupled two-spin system is irradiated selectively by a shaped RF pulse. In this case, we can see from equations (5) that the two sets of the rotation parameters corresponding to the DQ and ZQ contributions are completely equivalent, $(\alpha_\Sigma, \beta_\Sigma, \gamma_\Sigma) = (\alpha_\Delta, \beta_\Delta, \gamma_\Delta) \equiv (\alpha, \beta, \gamma)$ or $(a_\Sigma, b_\Sigma, c_\Sigma, d_\Sigma) = (a_\Delta, b_\Delta, c_\Delta, d_\Delta) \equiv (a, b, c, d)$. Consequently, according to table 4 we have

$$I_z \xrightarrow{U} (c^2+d^2-a^2-b^2)I_z - 2(ad+bc)I_y - 2(ac-bd)2I_xS_z$$
$$= \cos\beta I_z - \sin\beta\sin\gamma I_y + \sin\beta\cos\gamma 2I_xS_z, \quad (15a)$$
$$S_z \xrightarrow{U} S_z. \quad (15b)$$

Not surprisingly, the antiphase magnetization of the irradiated spin I, $2I_xS_z$, can appear from the equilibrium state.

For the other special case, consider two equal, $\omega_{1I}(t) = \omega_{1S}(t)$, amplitude modulated RF pulses simultaneously applied along the x axis on two coupled spins. The three Euler angles for the ZQ contribution are found to be

$$\alpha_\Delta = -\frac{\pi}{2} - \frac{\pi J\Delta T}{2}, \quad \beta_\Delta = 0, \quad \gamma_\Delta = \frac{\pi}{2} - \frac{\pi J \Delta T}{2}, \quad (16)$$

so the quaternion elements are obtained from equation (13) to be

$$a_\Delta = b_\Delta = 0, \quad c_\Delta = -\sin\frac{\pi J\Delta T}{2}, \quad d_\Delta = \cos\frac{\pi J \Delta T}{2}, \quad (17)$$

where ΔT is the pulse duration. Using the evolution expressions in table 4, we have

$$I_z \xrightarrow{U} (c_\Delta c_\Sigma + d_\Delta d_\Sigma)I_z - (c_\Delta b_\Sigma + d_\Delta a_\Sigma)I_y - (c_\Delta d_\Sigma - d_\Delta c_\Sigma)2I_xS_y - (c_\Delta a_\Sigma - d_\Delta b_\Sigma)2I_xS_z, \quad (18a)$$

$$S_z \xrightarrow{U} (c_\Delta c_\Sigma + d_\Delta d_\Sigma)S_z - (c_\Delta b_\Sigma + d_\Delta a_\Sigma)S_y - (c_\Delta d_\Sigma - d_\Delta c_\Sigma)2I_yS_x - (c_\Delta a_\Sigma - d_\Delta b_\Sigma)2I_zS_x, \quad (18b)$$

whose four coefficients can be expressed further using equations (16) and (17) to give

$$c_z = c_\Delta c_\Sigma + d_\Delta d_\Sigma = \cos\left(\frac{\pi J\Delta T + \gamma_\Sigma + \alpha_\Sigma}{2}\right)\cos\frac{\beta_\Sigma}{2}, \quad (19a)$$

$$c_y = -c_\Delta b_\Sigma - d_\Delta a_\Sigma = \sin\left(\frac{\pi J\Delta T - \gamma_\Sigma + \alpha_\Sigma}{2}\right)\sin\frac{\beta_\Sigma}{2}, \quad (19b)$$

$$c_{xy} = -c_\Delta d_\Sigma + d_\Delta c_\Sigma = \sin\left(\frac{\pi J \Delta T + \gamma_\Sigma + \alpha_\Sigma}{2}\right)\cos\frac{\beta_\Sigma}{2}, \tag{19c}$$

$$c_{xz} = -c_\Delta a_\Sigma + d_\Delta b_\Sigma = \cos\left(\frac{\pi J \Delta T - \gamma_\Sigma + \alpha_\Sigma}{2}\right)\sin\frac{\beta_\Sigma}{2}. \tag{19d}$$

Equations (18) together with (19) describe the response of a coupled two-spin system originally at equilibrium to two on-resonance amplitude modulated RF pulses. In order to obtain the DQ rotation parameters which arise in the evolution, a numerical method is described below.

4. Numerical calculation

It can be demonstrated readily [14, 15] that the result $(a_{tot}, b_{tot}, c_{tot}, d_{tot})$ of two consecutive rotations (a_2, b_2, c_2, d_2) and (a_1, b_1, c_1, d_1) may be represented by

$$\begin{bmatrix} a_{tot} \\ b_{tot} \\ c_{tot} \\ d_{tot} \end{bmatrix} = \begin{bmatrix} d_2 & c_2 & -b_2 & a_2 \\ -c_2 & d_2 & a_2 & b_2 \\ b_2 & -a_2 & d_2 & c_2 \\ -a_2 & -b_2 & -c_2 & d_2 \end{bmatrix} \begin{bmatrix} a_1 \\ b_1 \\ c_1 \\ d_1 \end{bmatrix}. \tag{20}$$

According to equation (5*a*), the small rotation caused by the DQ contribution during a short interval Δt at an arbitrary time t_i can be expressed as

$$\Delta a_i = \frac{\omega(t_i)}{\Omega(t_i)}\sin\frac{\Omega(t_i)\,\Delta t}{2}, \tag{21a}$$

$$\Delta b_i = 0, \tag{21b}$$

$$\Delta c_i = -\frac{\pi J}{\Omega(t_i)}\sin\frac{\Omega(t_i)\,\Delta t}{2}, \tag{21c}$$

$$\Delta d_i = \cos\frac{\Omega(t_i)\,\Delta t}{2}, \tag{21d}$$

where $\Omega(t_i) = (\omega(t_i)^2 + (\pi J)^2)^{1/2}$. Note that, for clarity, the subscript Σ specifying the DQ contribution has been dropped. The rotation composition rule (20), combined with equations (21) and the initial rotation parameters $a(0) = b(0) = c(0) = 0$ and $d(0) = 1$, yields an effective and relatively simple method for the numerical evaluation of the total rotation parameters, the three Euler angles and the quaternion elements. This provides an alternative procedure to that of solving the Euler geometric equations [3]. From the definition of quaternion elements, we have

$$\cos\beta = 1 - 2(a^2 + b^2) = 2(c^2 + d^2) - 1, \tag{22a}$$

$$\alpha = \tan^{-1}\left(\frac{c}{d}\right) - \tan^{-1}\left(\frac{a}{b}\right), \tag{22b}$$

$$\gamma = \tan^{-1}\left(\frac{c}{d}\right) + \tan^{-1}\left(\frac{a}{b}\right), \tag{22c}$$

which can be used to derive the Euler angles from the quaternion elements.

Let us consider again the second particular case in section 3, of simultaneous

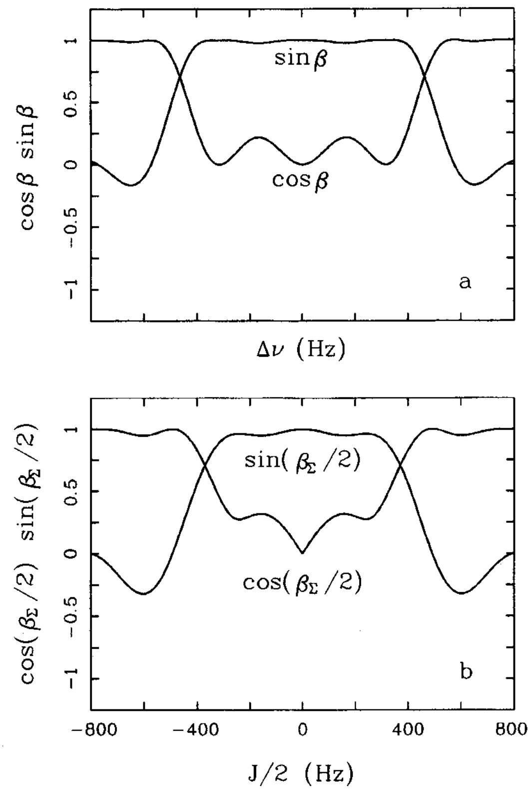

Figure 1. (*a*) Profiles of two factors $\cos\beta$ and $\sin\beta$ for a $\pi/2$ sinc-shaped pulse (truncation at the third zero; duration of 6 ms) as functions of the resonance offset $\Delta\nu$, and (*b*) profiles of two half-angle factors $\cos\beta_\Sigma/2$ and $\sin\beta_\Sigma/2$ for two identical $\pi/2$ sinc-shaped pulses as functions of the quantity $J/2$.

irradiation by a pair of equal amplitude modulated RF pulses along the x axis. It can be seen from equation (5*a*) that the profiles of the three Euler angles (or the quaternion elements) for the DQ contribution with a quantity $J/2$ are completely equivalent to those of the same rotation parameters with a resonance offest $\Delta\nu$ for an isolated spin system subject to an RF pulse with the same shape but twice the strength. Note that the four coefficients (19) contain two half-angle terms $\cos\beta_\Sigma/2$ and $\sin\beta_\Sigma/2$ while these two factors are obviously different from $\cos\beta$ and $\sin\beta$ characterizing the RF pulses applied originally [3], as illustrated in figure 1 for $\pi/2$ sinc-shaped RF pulses. In practice, a $\pi/2$ sinc-shaped pulse with double strength is exactly a π sinc-shaped pulse, so β_Σ is the Euler angle for a π shaped RF pulse.

Figure 2 is a plot of the four terms c_z, c_y, c_{xy}, and c_{xz} for two identical E-BURP-2 pulses [16] as a function of $J/2$. It is apparent that its right-half part is equivalent to that corresponding to $J\Delta T$ from 0 to 20 in [8], figure 1. Additionally, a plot for two equal half-amplitude I-BURP-2 pulses [16] is shown in figure 3, where half amplitude means that all Fourier coefficients listed in [16], table 6 are divided by two, for instance, $A_0 = 0{\cdot}25$, $A_1 = 0{\cdot}405$ and $B_1 = -0{\cdot}34$ for $N_p = 256$. As was expected, the profiles obtained can be compared with those in [16], figure 9. Since the E-BURP-2 and half-amplitude I-BURP-2 pulses are not the same, there is an evident difference between figure 2 and figure 3. This may be important for the analysis and design of shaped RF pulses applied to coupled spin systems.

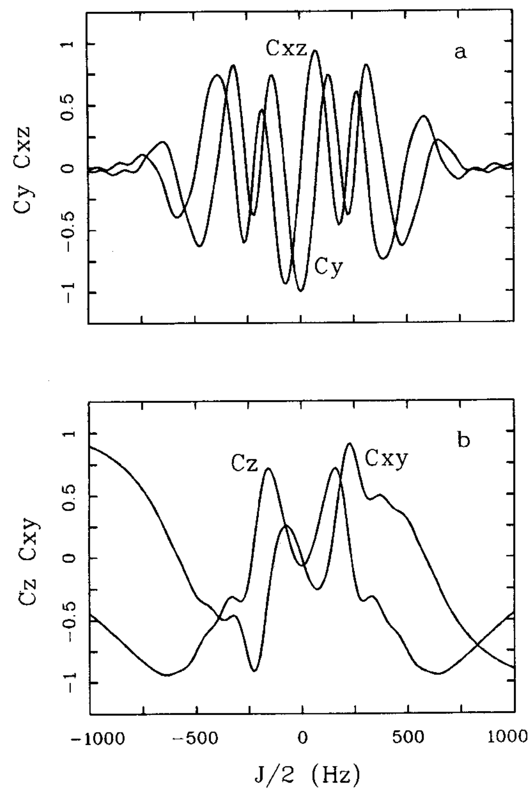

Figure 2. Plot of four terms (*a*) c_y, c_{xz} and (*b*) c_z, c_{xy} for two equal E-BURP-2 pulses (duration of 10 ms) as a function of the quantity J/2.

In the case of real time-symmetrical RF pulses, such as sinc and Gaussian shapes, applied along the x axis, the total rotation parameter b is zero, i.e., $\gamma-\alpha=\pi$ corresponding to the form of equation (5), for all resonance offsets [15]. In addition, for the situation of simultaneous irradiation by two arbitrary RF pulses, we can always write $\gamma_\Sigma+\alpha_\Sigma=-\pi J\Delta T+\varepsilon$, where ε is a number dependent on the scalar-coupling coefficients and the shapes of applied RF pulses. Equation (19) can thus be rewritten as

$$c_z = \cos\varepsilon\cos\frac{\beta_\Sigma}{2}, \tag{23a}$$

$$c_y = -\cos\left(\frac{\pi J\Delta T}{2}\right)\sin\frac{\beta_\Sigma}{2}, \tag{23b}$$

$$c_{xy} = \sin\varepsilon\cos\frac{\beta_\Sigma}{2}, \tag{23c}$$

$$c_{xz} = \sin\left(\frac{\pi J\Delta T}{2}\right)\sin\frac{\beta_\Sigma}{2}. \tag{23d}$$

Note that equations (23*b*, *d*) are suitable only for the special case of two equal $\pi/2$ time-symmetrical amplitude modulated RF pulses applied simultaneously along the x axis on two coupled spins. Figure 4 illustrates the profiles of these coefficients for two

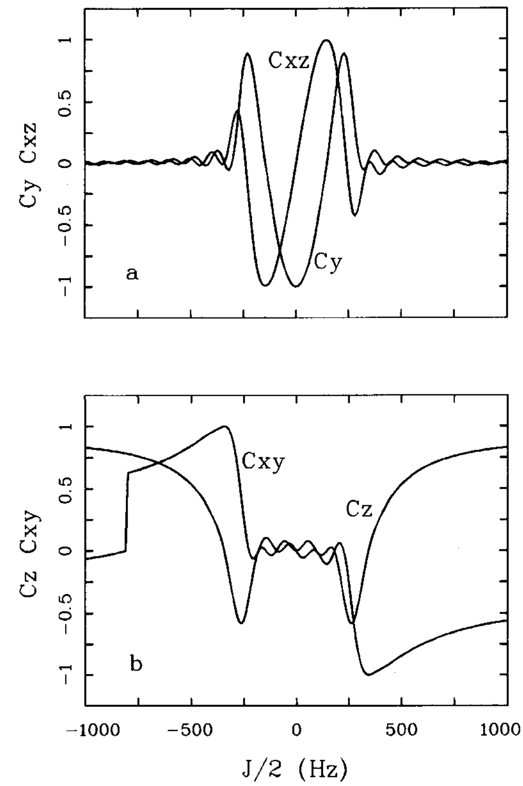

Figure 3. Plot of four terms (*a*) c_y, c_{xz} and (*b*) c_z, c_{xy} for two equal half-amplitude I-BURP-2 pulses (duration of 10 ms) as a function of $J/2$.

identical $\pi/2$ sinc-shaped RF pulses as functions of the quantity $J/2$. Obviously the use of figure 1(*b*) together with equations (23) provides an intuitive insight into the calculated profiles.

5. Conclusion

Using the rotation operator approach as well as routine procedures, we have examined the evolution behaviour of a weakly scalar-coupled two-spin system under the influence of two amplitude modulated RF pulses at resonance. Instead of a numerical calculation directly with the Liouville–von Neumann equation used commonly [4, 6, 8], our analytical description should be useful for rationalizing the essential features of such a doubly amplitude modulated spin problem. We believe that in comparison with other approaches [7] our formulation introduces another perspective which provides a relatively simple visualization of simultaneous commuting rotations. In addition, our theory gives an amenable starting point for further numerical calculation.

Finally, we would like to mention that the theory given in this paper is also capable of treating heteronuclear cross-polarization dynamics in rotating solids [17], based on the simple model of isolated two-spin systems frequently employed.

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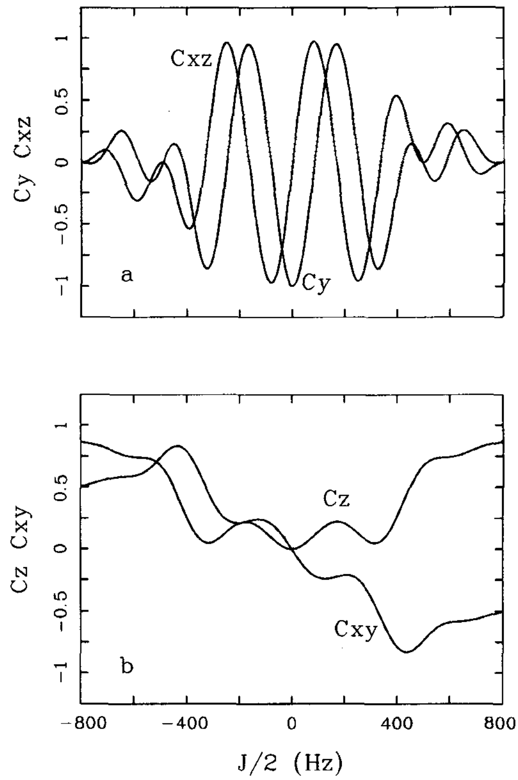

Figure 4. Profiles of four coefficients (*a*) c_y, c_{xz} and (*b*) c_z, c_{xy} for two equal $\pi/2$ sinc-shaped RF pulses (truncation at the third zero; duration of 6 ms) as functions of $J/2$.

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