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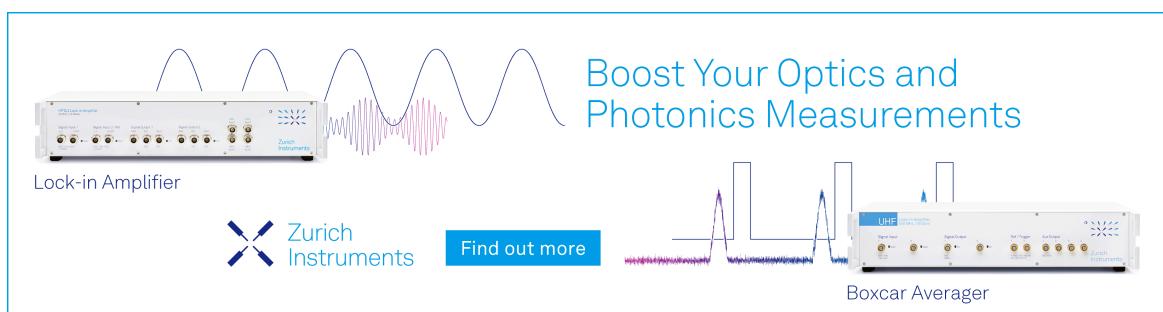
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Selective excitation and detection in multilevel spin systems: Application of single transition operators

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An alternative definition of single transition operators is given for the description of selective excitation and detection experiments in multilevel spin systems. This definition has the virtues of a simple physical interpretation and easy application to arbitrarily complicated systems. Some applications to the excitation and detection of multiple quantum transitions in spin 1 and spin 3/2 systems as well as in coupled spin systems are described.

I. INTRODUCTION

In the past years a multitude of selective excitation and detection techniques has been developed in various kinds of coherent spectroscopies, ranging from radio-frequency spectroscopy to optical spectroscopy. Outstanding examples are the selective excitation of single quantum transitions¹ and multiple quantum transitions² in continuous wave magnetic resonance, selective double resonance in magnetic resonance,³ selective pulse experiments in high resolution NMR,⁴ laser spectroscopy,⁵ and selective optical pulse experiments.⁶

In all these examples one or at maximum a few well chosen transitions are excited selectively, and the same or another set of transitions is being observed subsequently. The appropriate tools to theoretically describe such experiments appear to be single transition operators, which permit a convenient formulation of selective excitation and detection processes.

The scope of this paper will be limited to magnetic resonance although there are many important applications particularly in coherent optical spectroscopy. Several proposals to describe selective magnetic resonance experiments by single transition operators have been made in the past. An important early example is the description of the behavior of a "simple" line by Bloch-type equations by Abragam.¹ This concept of classical description of a quantum mechanical subsystem has recently been extended by Hahn and co-workers⁷ to three-level systems.

The most recent contribution, which also initiated the work to be described in the present paper, has been made by Vega and Pines,⁸ who applied fictitious spin $\frac{1}{2}$ operators for the description of double quantum NMR for spin 1 systems. In a basic study^{8(c)} they presented a thorough discussion of the most relevant aspects of double quantum NMR in terms of single transition operators.

The aim of the present paper is to present an alternative possibility for the definition of single transition operators, which appear to us to possess several advantages over the definition given by Vega and Pines. Particularly, there is a more natural connection to the concepts of macroscopic magnetization vectors. The definition is also of great generality and can easily be applied to arbitrary systems containing an arbitrary

number of spins with arbitrary spin quantum numbers.

The definition and description of the proposed single transition operators are given in Sec. II. Applications to double quantum NMR of spin 1 systems are described in Sec. III. In Sec. IV some results for spin $\frac{3}{2}$ are presented and, finally, Sec. V is devoted to a simple application of single transition operators to coupled systems of spins $\frac{1}{2}$. A more extensive discussion of multiple quantum transitions in coupled spin systems will be presented in another place.

II. DEFINITION OF SINGLE TRANSITION OPERATORS

Let ψ_r and ψ_s be two eigenstates of the considered spin system. The single transition operators associated with the transition $r \rightarrow s$, which may represent a zero-, single- or multiple-quantum transition, are defined in the following way:

$$\begin{aligned} \langle \psi_i | I_x^{(rs)} | \psi_f \rangle &= 1/2(\delta_{ir} \delta_{js} + \delta_{is} \delta_{jr}) , \\ \langle \psi_i | I_y^{(rs)} | \psi_f \rangle &= i/2(-\delta_{ir} \delta_{js} + \delta_{is} \delta_{jr}) , \\ \langle \psi_i | I_z^{(rs)} | \psi_f \rangle &= 1/2(\delta_{ir} \delta_{jr} - \delta_{is} \delta_{js}) . \end{aligned} \quad (1)$$

From these definitions it follows that for the transition $s \rightarrow r$

$$\begin{aligned} I_x^{(sr)} &= I_x^{(rs)} , \\ I_y^{(sr)} &= -I_y^{(rs)} , \\ I_z^{(sr)} &= -I_z^{(rs)} . \end{aligned} \quad (2)$$

The three operators belonging to one particular transition $r \rightarrow s$ obey standard commutation relationships

$$[I_\alpha^{(rs)}, I_\beta^{(rs)}] = i I_\gamma^{(rs)} , \quad (3)$$

where (α, β, γ) is a cyclic permutation of (x, y, z) .

For the operators describing two connected transitions $r \rightarrow t$ and $s \rightarrow t$ (with the states ψ_r , ψ_s , and ψ_t all distinct) the following commutation rules hold:

$$\begin{aligned} [I_x^{(rt)}, I_x^{(st)}] &= [I_y^{(rt)}, I_y^{(st)}] = i/2 I_y^{(rs)} , \\ [I_z^{(rt)}, I_z^{(st)}] &= 0 , \\ [I_x^{(rt)}, I_y^{(st)}] &= i/2 I_x^{(rs)} , \\ [I_x^{(rt)}, I_z^{(st)}] &= -i/2 I_y^{(rs)} , \\ [I_y^{(rt)}, I_z^{(st)}] &= i/2 I_x^{(rs)} . \end{aligned} \quad (4)$$

It is important to note the order of the states in the

labels of the operators; changing this order results in sign changes according to Eq. (2), e.g.,

$$[I_x^{(rs)}, I_y^{(ts)}] = -i/2 I_x^{(rs)}.$$

Operators belonging to nonconnected transitions do always commute,

$$[I_\alpha^{(rs)}, I_\beta^{(tu)}] = 0, \quad \begin{cases} \alpha \\ \beta \end{cases} = x, y, z. \quad (5)$$

It should be noted that there are linear dependences among the z components,

$$I_z^{(rs)} + I_z^{(st)} + I_z^{(tr)} = 0. \quad (6)$$

The observable operators $I_x, I_y, I_z, F_x, F_y, F_z$, respectively for multispin systems, can easily be expressed by the defined single transition operators. For a one-spin system with spin I and a Hamiltonian commuting with I_z , one obtains

$$I_{x,y} = \sum_{(rs)1} \sqrt{c^{(rs)}} I_{x,y}^{(rs)}, \quad (7)$$

$$I_z = \sum_{(rs)1} c^{(rs)} I_z^{(rs)} \quad (8)$$

with

$$c^{(rs)} = I(I+1) - m_r m_s, \quad (9)$$

where m_r and m_s are the magnetic quantum numbers of the involved states. The summation runs over all ordered⁹ pairs of single quantum transitions. For a weakly coupled multi-spin 1/2 system one obtains simply

$$F_\alpha = \sum_{(rs)1} I_\alpha^{(rs)}, \quad \alpha = x, y, z. \quad (10)$$

III. APPLICATION OF SINGLE TRANSITION OPERATORS TO AN ISOLATED SPIN $I=1$ WITH QUADRUPOLAR INTERACTION

The utility of single transition operators will be illustrated by applications to selective pulse experiments on noninteracting spins $I=1$ subject to a strong static magnetic field B_0 and to quadrupolar interaction. These applications are relevant in view of the newly developed techniques of double quantum spectroscopy by Vega and Pines⁸ and by Hashi.¹⁰

A. Free precession without rf irradiation

The Hamiltonian in the laboratory frame is chosen as

$$\mathcal{H} = \omega_0 I_z + \frac{\omega_Q}{3} [3 I_z^2 - I(I+1)], \quad (11)$$

where ω_Q is the quadrupolar splitting parameter of the single quantum spectrum. Transformation into a coordinate system rotating at the detection frequency ω_r leads to the rotating frame Hamiltonian

$$\mathcal{H}_r = \Delta \omega_0 I_z + \frac{\omega_Q}{3} [3 I_z^2 - I(I+1)], \quad (12)$$

with

$$\Delta \omega_0 = \omega_0 - \omega_r. \quad (13)$$

For the operator base, the nine operators $\{I_\alpha^{(12)}, I_\alpha^{(23)}, I_\alpha^{(13)}; \alpha = x, y, z\}$ supplemented by the unity matrix 1 are chosen. The three z operators are linearly de-

pendent by the relation

$$I_z^{(12)} + I_z^{(23)} + I_z^{(13)} = 0. \quad (14)$$

The single transition operators are in this case related to the fictitious spin 1/2 operators $I_{\alpha,k}$, $\alpha = x, y, z$, $k = 1, 2, 3$, defined by Vega and Pines,⁸ in the following manner:

$$\begin{aligned} I_{x,1} &= 2^{-1/2} (I_x^{(12)} + I_x^{(23)}), \\ I_{x,2} &= 2^{-1/2} (I_x^{(12)} - I_x^{(23)}), \\ I_{x,3} &= 2^{-1} (I_x^{(13)} + I_x^{(12)} - I_x^{(23)}), \\ I_{y,1} &= 2^{-1/2} (I_y^{(12)} + I_y^{(23)}), \\ I_{y,2} &= 2^{-1/2} (I_y^{(12)} - I_y^{(23)}), \\ I_{y,3} &= 2^{-1} (I_y^{(13)} - I_y^{(12)} + I_y^{(23)}), \\ I_{z,1} &= I_z^{(13)}, \\ I_{z,2} &= I_z^{(13)}, \\ I_{z,3} &= -I_z^{(13)}. \end{aligned} \quad (15)$$

From these equations it is seen that $I_{x,k}$ and $I_{y,k}$ are linear combinations of operators belonging to different transitions. Consequently, the matrix representations $I_{x,k}^t$ and $I_{y,k}^t$ in the eigenbase of I_z , $\{\psi_1, \psi_0, \psi_{-1}\}$, contain more than two matrix elements different from zero.

However, the unitary transformation

$$I_{\alpha,k}^X = T^{-1} I_{\alpha,k}^t T, \quad (16)$$

where T describes the base transformation into the eigenbase of I_z^2 ,

$$\{\chi_1 \chi_2 \chi_3\} = \{\psi_1 \psi_0 \psi_{-1}\} T = \{\psi_1 \psi_0 \psi_{-1}\} \begin{pmatrix} -\frac{i}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \\ \frac{i}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \end{pmatrix}, \quad (17)$$

generates matrices $I_{\alpha,k}^X$, each of which contains only two nonvanishing matrix elements. Thus, there exists a formal similarity between the set of matrix representations $\{I_\alpha^{(12)t}, I_\alpha^{(23)t}, I_\alpha^{(13)t}; \alpha = x, y, z\}$ in the eigenbase of I_z , and the set of matrix representations $\{I_{\alpha,k}^X; \alpha = x, y, z, k = 1, 2, 3\}$ in the eigenbase of I_z^2 [listed in Table II of Ref. 8(c)]. However, the operators themselves are physically different, and related by Eqs. (15). In the case of high field NMR the set $\{I_\alpha^{(rs)t}\}$ is more appropriate as operator base and leads to an easier visualization, whereas for pure quadrupole resonance the set $\{I_{\alpha,k}\}$ is better adapted.

The density matrix in the rotating frame $\rho(t)$ and the Hamiltonian \mathcal{H}_r are now expanded in the base $\{I_\alpha^{(rs)t}\}$:

$$\begin{aligned} \rho(t) &= c_0 \mathbf{1} + \sum_{\alpha=x,y,z} (c_\alpha^{(12)}(t) I_\alpha^{(12)} \\ &\quad + c_\alpha^{(23)}(t) I_\alpha^{(23)} + c_\alpha^{(13)}(t) I_\alpha^{(13)}), \end{aligned} \quad (18)$$

$$\mathcal{H}_r = \Delta \omega_0 (I_z^{(12)} + I_z^{(23)} + I_z^{(13)}) + \frac{2\omega_Q}{3} (I_z^{(12)} - I_z^{(23)}). \quad (19)$$

Insertion of the expansion (18) into the density operator

equation

$$\dot{\rho}(t) = -i[\mathcal{H}_r, \rho(t)] \quad (20)$$

and use of the commutation relations (3) and (4) then leads to the following closed solution for the coefficients $c_{\alpha}^{(ij)}(t)$:

$$\begin{aligned} c_x^{(ij)}(t) &= c_x^{(ij)}(0) \cos \omega_{ij} t - c_y^{(ij)}(0) \sin \omega_{ij} t, \\ c_y^{(ij)}(t) &= c_x^{(ij)}(0) \sin \omega_{ij} t + c_y^{(ij)}(0) \cos \omega_{ij} t, \\ c_z^{(ij)}(t) &= c_z^{(ij)}(0), \end{aligned} \quad (21)$$

with

$$\omega_{ij} = (\mathcal{H}_r)_{ii} - (\mathcal{H}_r)_{jj}. \quad (22)$$

Equations (21) can be interpreted as a precession of the transverse magnetization components of transition (ij) about the z axis. In connection with double quantum spectroscopy^{8,11} it is to be noted that the double quantum expectation values $\langle I_x^{(13)} \rangle(t)$ and $\langle I_y^{(13)} \rangle(t)$ precess at $\omega_{13} = 2\Delta\omega_0$ and are not influenced by the quadrupolar interaction.

The general result of Eqs. (21) constitutes a considerable simplification as compared to the corresponding solution in the operator base $\{I_{\alpha, \beta}\}$, given by Vega and Pines [Ref. 8(c), Eq. (69)], where an assumption on the vanishing of three coefficients at time $t=0$ had to be made to obtain simple expressions, and where the magnetization components of the "x frame" and "y frame"⁸ are mixed during time evolution.

B. Irradiation near a single quantum transition

To excite the single quantum transition $1-2$ at frequency $\omega_0 + \omega_Q$, ω_r is chosen as

$$\omega_r = \omega_0 + \omega_Q - \delta\omega, \quad (23)$$

such that

$$\Delta\omega_0 = \omega_0 - \omega_r = -\omega_Q + \delta\omega. \quad (24)$$

The Hamiltonian in the rotating frame then becomes

$$\begin{aligned} \mathcal{H}_r &= (-\omega_Q + \delta\omega)(I_z^{(12)} + I_z^{(23)} + I_z^{(13)}) \\ &+ \frac{2}{3}\omega_Q(I_z^{(12)} - I_z^{(23)}) + \omega_1 \sqrt{2}(I_x^{(12)} + I_x^{(23)}). \end{aligned} \quad (25)$$

For $\omega_1 = 0$ the eigenvalues are given by

$$\begin{aligned} (\mathcal{H}_r)_{11} &= -\frac{2}{3}\omega_Q + \delta\omega, \\ (\mathcal{H}_r)_{22} &= -\frac{2}{3}\omega_Q, \\ (\mathcal{H}_r)_{33} &= +\frac{4}{3}\omega_Q - \delta\omega. \end{aligned} \quad (26)$$

If the condition $\omega_1 \ll \omega_Q$ is satisfied, the operator $\omega_1 \sqrt{2} I_x^{(23)}$ can be omitted, as its off-diagonal elements connect the levels ψ_2 and ψ_3 separated by an energy difference of $2\omega_Q$. Rearranging the remaining terms one arrives at the following representation of \mathcal{H}_r :

$$\begin{aligned} \mathcal{H}_r &= \mathcal{H}_1 + \mathcal{H}_2, \\ \mathcal{H}_1 &= \delta\omega I_z^{(12)} + \omega_1 \sqrt{2} I_x^{(12)}, \\ \mathcal{H}_2 &= -\left(\frac{4}{3}\omega_Q - \delta\omega\right)(I_z^{(23)} + I_z^{(13)}), \\ [\mathcal{H}_1, \mathcal{H}_2] &= 0. \end{aligned} \quad (27)$$

\mathcal{H}_1 is the familiar Hamiltonian of a two-level system irradiated with a rotating rf field with amplitude $\omega_1 \sqrt{2}$

and with resonance offset $\delta\omega$. The factor $\sqrt{2}$ originates from the matrix element of I_x , which, for $I=1$, is a factor of $\sqrt{2}$ larger than that for $I=1/2$.

To calculate the time development of the density matrix during a selective single quantum pulse acting on transition (12) alone, \mathcal{H}_1 is diagonalized by a rotation about the $y^{(12)}$ axis through an angle θ , with

$$\tan\theta = \omega_1 \sqrt{2}/\delta\omega. \quad (28)$$

One obtains

$$\mathcal{H}_{1T} = T^{-1} \mathcal{H}_1 T = \omega_{\text{eff}} I_z^{(12)}, \quad (29)$$

where

$$T = \exp(-i\theta I_y^{(12)}) \quad (30)$$

and

$$\omega_{\text{eff}} = (\delta\omega^2 + 2\omega_1^2)^{1/2}. \quad (31)$$

\mathcal{H}_2 remains invariant under the rotation T of the (12) coordinate system.

The effect of the single quantum pulse on a spin system in thermodynamic equilibrium can now easily be calculated. The equilibrium density matrix is written

$$\rho_0 = b\{I_z^{(12)} + I_z^{(23)} + I_z^{(13)}\}, \quad (32)$$

omitting the term proportional to the unity matrix and defining b as $-\omega_0/kT$. Performing the rotation about the $y^{(12)}$ axis leads to

$$\rho_T(0) = b\{(I_z^{(12)} \cos\theta - I_x^{(12)} \sin\theta) + (I_z^{(23)} + I_z^{(13)})\}. \quad (33)$$

The time development is calculated with the Hamiltonian (29), and the resulting density matrix $\rho_T(t)$ transformed back into the original frame, yielding

$$\begin{aligned} \rho(t) &= b\{I_z^{(12)}(\cos^2\theta + \sin^2\theta \cos\omega_{\text{eff}}t) + I_x^{(12)} \frac{1}{2} \sin 2\theta \\ &\times (1 - \cos\omega_{\text{eff}}t) - I_y^{(12)} \sin\theta \sin\omega_{\text{eff}}t + (I_z^{(23)} + I_z^{(13)})\}. \end{aligned} \quad (34)$$

The pulse has generated only transverse (12) magnetization, while the (23) and (13) magnetization components have remained parallel to the z axis.

C. Irradiation near the double quantum transition

At first the irradiation frequency is chosen exactly in the center of the spectrum, i.e., $\Delta\omega_0 = 0$. The Hamiltonian is then given by

$$\mathcal{H}_r = \frac{2}{3}\omega_Q(I_z^{(12)} - I_z^{(23)}) + \omega_1 \sqrt{2}(I_x^{(12)} + I_x^{(23)}). \quad (35)$$

\mathcal{H}_r is diagonalized by the orthogonal transformation

$$\mathcal{H}_{rT} = T^{-1} \mathcal{H}_r T, \quad (36)$$

with

$$T = \begin{pmatrix} \frac{1}{\sqrt{2}} \cos\theta/2 & -\frac{1}{\sqrt{2}} \sin\theta/2 & -\frac{1}{\sqrt{2}} \\ \sin\theta/2 & \cos\theta/2 & 0 \\ \frac{1}{\sqrt{2}} \cos\theta/2 & -\frac{1}{\sqrt{2}} \sin\theta/2 & \frac{1}{\sqrt{2}} \end{pmatrix}, \quad (37)$$

$$\tan\theta = 2\omega_1/\omega_Q. \quad (38)$$

The eigenvalues are given by

$$\begin{aligned} (\mathcal{H}_{rT})_{11} &= -\frac{1}{6}\omega_Q + \frac{1}{2}\omega_e, \\ (\mathcal{H}_{rT})_{22} &= -\frac{1}{6}\omega_Q - \frac{1}{2}\omega_e, \\ (\mathcal{H}_{rT})_{33} &= +\frac{1}{3}\omega_Q, \end{aligned} \quad (39)$$

with

$$\omega_e = (\omega_Q^2 + 4\omega_1^2)^{1/2}. \quad (40)$$

Because of the linear dependence, Eq. (14), the operator representation of \mathcal{H}_{rT} is not uniquely determined.

Two forms will prove useful in the following:

$$\mathcal{H}_{rT} = \frac{1}{2}(\omega_e - \omega_Q)I_x^{(13)} + (\frac{1}{2}\omega_e + \frac{1}{6}\omega_Q)(I_x^{(12)} - I_x^{(23)}) \quad (41)$$

$$= -\frac{1}{2}(\omega_e + \omega_Q)I_x^{(23)} + (\frac{1}{2}\omega_e - \frac{1}{6}\omega_Q)(I_x^{(12)} + I_x^{(13)}). \quad (42)$$

$$\rho_T(t) = -2b\{\cos\theta/2[I_x^{(13)}\cos\frac{1}{2}(\omega_e - \omega_Q)t + I_y^{(13)}\sin\frac{1}{2}(\omega_e - \omega_Q)t] - \sin\theta/2[I_x^{(23)}\cos\frac{1}{2}(\omega_e + \omega_Q)t - I_y^{(23)}\sin\frac{1}{2}(\omega_e + \omega_Q)t]\}. \quad (45)$$

Transformation back into the original frame yields

$$\rho(t) = 2b\{I_x^{(13)}[\cos^2\theta/2\cos\frac{1}{2}(\omega_e - \omega_Q)t + \sin^2\theta/2\cos\frac{1}{2}(\omega_e + \omega_Q)t] - I_y^{(13)}[\cos^2\theta/2\sin\frac{1}{2}(\omega_e - \omega_Q)t - \sin^2\theta/2\sin\frac{1}{2}(\omega_e + \omega_Q)t]\}$$

$$- \frac{1}{2\sqrt{2}}\sin\theta(I_y^{(12)} + I_y^{(23)})[\sin\frac{1}{2}(\omega_e - \omega_Q)t + \sin\frac{1}{2}(\omega_e + \omega_Q)t] - \frac{1}{2\sqrt{2}}\sin\theta(I_x^{(12)} - I_x^{(23)})[-\cos\frac{1}{2}(\omega_e - \omega_Q)t + \cos\frac{1}{2}(\omega_e + \omega_Q)t]\}. \quad (46)$$

For a selective double quantum pulse $\omega_1 \ll \omega_Q$ the general solution can be considerably simplified using $\theta \approx 0$ and expanding the square root to give

$$\frac{1}{2}(\omega_e - \omega_Q) \approx \omega_1^2/\omega_Q. \quad (47)$$

The result is

$$\rho(t) \approx 2b\left\{I_x^{(13)}\cos\frac{\omega_1^2}{\omega_Q}t - I_y^{(13)}\sin\frac{\omega_1^2}{\omega_Q}t\right\}. \quad (48)$$

Before the implications of Eqs. (46) and (48) are discussed the influence of a small resonance offset $\Delta\omega_0$ is considered. Transforming the Hamiltonian

$$\mathcal{H}_r = \Delta\omega_0 I_z + \frac{2\omega_Q}{3}(I_x^{(12)} - I_x^{(23)}) + \omega_1\sqrt{2}(I_x^{(12)} + I_x^{(23)}) \quad (49)$$

with the matrix T defined in Eq. (37) yields

$$\begin{aligned} \mathcal{H}_{rT} &= -2\Delta\omega_0(I_x^{(13)}\cos\theta/2 - I_x^{(23)}\sin\theta/2) \\ &+ \frac{1}{2}(\omega_e - \omega_Q)I_x^{(13)} + (\frac{1}{2}\omega_e + \frac{1}{6}\omega_Q)(I_x^{(12)} - I_x^{(23)}). \end{aligned} \quad (50)$$

It is illustrative to rotate the (13) axis system through an angle $-\pi/2$ about the $y^{(13)}$ axis. With

$$U = \exp\left(+i\frac{\pi}{2}I_y^{(13)}\right) \quad (51)$$

one obtains

$$\begin{aligned} \mathcal{H}_{rTU} &= U^{-1}\mathcal{H}_{rT}U \\ &= +2\Delta\omega_0[I_x^{(13)}\cos\theta/2 - (1/\sqrt{2})(I_x^{(12)} - I_x^{(23)})\sin\theta/2] \\ &+ \frac{1}{2}(\omega_e - \omega_Q)I_x^{(13)} + (\frac{1}{2}\omega_e + \frac{1}{6}\omega_Q)(I_x^{(12)} - I_x^{(23)}). \end{aligned} \quad (52)$$

Simplifying this Hamiltonian for $\omega_1 \ll \omega_Q$ yields

$$\begin{aligned} \mathcal{H}_{rTU} &\approx 2\Delta\omega_0I_x^{(13)} + (\omega_1^2/\omega_Q)I_x^{(13)} \\ &+ (\frac{1}{2}\omega_e + \frac{1}{6}\omega_Q)(I_x^{(12)} - I_x^{(23)}). \end{aligned} \quad (53)$$

The offset field along the $z^{(13)}$ axis is $2\Delta\omega_0$, a characteristic feature of the double quantum transition. The

To calculate the effect of a double quantum pulse on a spin system in thermodynamic equilibrium the density matrix

$$\rho_0 = b\{I_x^{(12)} + I_x^{(23)} + I_x^{(13)}\} = 2bI_x^{(13)} \quad (43)$$

is first subject to the transformation T , Eq. (37), yielding

$$\rho_T(0) = -2b\{I_x^{(13)}\cos\theta/2 - I_x^{(23)}\sin\theta/2\}. \quad (44)$$

Recognizing that $I_x^{(13)}$ commutes with $(I_x^{(12)} - I_x^{(23)})$ [in the first form of \mathcal{H}_{rT} , Eq. (41)], while $I_x^{(23)}$ commutes with $(I_x^{(12)} + I_x^{(13)})$ [in the second form of \mathcal{H}_{rT} , Eq. (42)], $\rho_T(t)$ is found to be

effective rf field ω_1^2/ω_Q points along the positive $x^{(13)}$ axis. For $\Delta\omega_0 = 0$ this field simply rotates the (13) magnetization about the $x^{(13)}$ axis. This is the physical interpretation of Eq. (48), which will now be rederived in a much shorter manner.

Since, for $\theta \approx 0$, $T \cdot U$ is approximately equal to the unity matrix, the initial condition is given by

$$\rho_{TU}(0) \approx \rho_0 = 2bI_x^{(13)}. \quad (54)$$

Since the last term of the Hamiltonian (53) commutes both with the rest of \mathcal{H}_{rTU} and with $I_x^{(13)}$, the density matrix evolves as

$$\begin{aligned} \rho(t) &\approx \rho_{TU}(t) \\ &\approx \exp\left(-i\frac{\omega_1^2}{\omega_Q}tI_x^{(13)}\right)2bI_x^{(13)}\exp\left(+i\frac{\omega_1^2}{\omega_Q}tI_x^{(13)}\right), \end{aligned} \quad (55)$$

which can be easily shown to be identical with Eq. (48).

A comparison with the results obtained by Vega and Pines is now in order. The diagonalizing matrix T in Eq. (37) can be represented as

$$T = \exp\left[-i\frac{\theta}{\sqrt{2}}(I_y^{(12)} - I_y^{(23)})\right]\exp\left(-i\frac{\pi}{2}I_y^{(13)}\right), \quad (56)$$

and, with the definition of U , Eq. (51), one finds

$$T \cdot U = \exp\left[-i\frac{\theta}{\sqrt{2}}(I_y^{(12)} - I_y^{(23)})\right]. \quad (57)$$

Noting that the sign of the rf field has been chosen in the opposite manner by Vega and Pines,⁸ and that, consequently, the sign of the angle θ must be changed when translating results of this work into the formalism of Ref. 8(c), the operator $T \cdot U$ turns out to be identical with $U_{x,2}$ used in Eq. (32) of Ref. 8(c). The Hamiltonian \mathcal{H}_{rTU} , Eq. (52), is equivalent to Eq. (42) of Ref. 8(c), and the density matrix after the double quantum pulse (46) corresponds to Eq. (89) of Ref. 8(c).

As shown by the Hamiltonian \mathcal{H}_{rTQ} , Eq. (53), and the solution for the density matrix, Eq. (48), the double quantum pulse can be treated as a two-level problem if $\omega_1 \ll \omega_Q$. This is an example for the "simple line" concept introduced by Abragam,¹ who shows that Bloch-type equations result for the relevant density matrix elements whenever the rf irradiation influences exclusively one transition in a spin system of arbitrary complexity.

This conclusion has recently also been reached by Gold and Hahn¹² in a different manner. Setting up differential equations for all density matrix elements in the three-level system of a spin $I=1$, and noting that the time derivatives of transverse single quantum magnetization components are small for selective irradiation in the center of the spectrum, they arrive at generalized Bloch equations for the three magnetization components of the double quantum transition.

IV. ISOLATED SPIN $I=3/2$ SUBJECT TO QUADRUPOLAR AND ZEEMAN INTERACTIONS

This section is intended to show that the single transition operators are equally useful for spin systems with $I > 1$. This is an advantage over the definitions given by Vega and Pines,⁸ which are designed specifically for $I=1$ and cannot easily be generalized. Suitable nuclei with $I=3/2$ for high field spectroscopy and for the observation of multiple quantum transitions are ⁷Li, ⁹Be, and ¹¹B.

The rotating frame Hamiltonian for a system of non-interacting $I=3/2$ nuclei is again given by

$$\mathcal{H}_r = \Delta\omega_0 I_z + \frac{1}{3}\omega_Q [3I_z^2 - I(I+1)] + \omega_1 I_x. \quad (58)$$

The eigenstates for $\omega_1=0$ are numbered in the order of decreasing magnetic quantum number, with the eigenvalues

$$\begin{aligned} E_1 &= \frac{3}{2}\Delta\omega_0 + \omega_Q, \\ E_2 &= \frac{1}{2}\Delta\omega_0 - \omega_Q, \\ E_3 &= -\frac{1}{2}\Delta\omega_0 - \omega_Q, \\ E_4 &= -\frac{3}{2}\Delta\omega_0 + \omega_Q. \end{aligned} \quad (59)$$

The single quantum spectrum consists of three lines at frequencies $\omega_0 - 2\omega_Q$, ω_0 , and $\omega_0 + 2\omega_Q$. The double quantum transitions occur at frequencies $\omega_0 - \omega_Q$ and $\omega_0 + \omega_Q$, which, in contrast to the $I=1$ case discussed in Sec. III, depend on the quadrupolar splitting ω_Q . Therefore, selective excitation of a double quantum transition

will only be possible for a single crystal sample with one or several discrete values of ω_Q . The ω_Q -independent triple quantum transition, at frequency ω_0 , coincides with the center line of the single quantum spectrum.

A. Selective excitation of a double quantum transition

With the choice $\Delta\omega_0 = -\omega_Q$ the energy eigenvalues become

$$\begin{aligned} E_1 &= E_3 = -\frac{1}{2}\omega_Q, \\ E_2 &= -\frac{3}{2}\omega_Q, \\ E_4 &= +\frac{5}{2}\omega_Q. \end{aligned} \quad (60)$$

I_x in Eq. (58) is now decomposed into single transition operators

$$I_x = \sqrt{3}(I_x^{(12)} + I_x^{(34)}) + 2I_x^{(23)}. \quad (61)$$

Because $(E_4 - E_3) = 3(E_1 - E_2) = 3(E_3 - E_2)$, the influence of the operators $I_x^{(12)}$ and $I_x^{(23)}$ is considerably stronger than that of $I_x^{(34)}$, such that the latter can be neglected for $\omega_1 \ll \omega_Q$. \mathcal{H}_r is then diagonalized by the matrix

$$T = \begin{pmatrix} \sqrt{\frac{3}{7}}\cos\theta/2 & -\sqrt{\frac{3}{7}}\sin\theta/2 & -\frac{2}{\sqrt{7}} & 0 \\ \sin\theta/2 & \cos\theta/2 & 0 & 0 \\ \frac{2}{\sqrt{7}}\cos\theta/2 & -\frac{2}{\sqrt{7}}\sin\theta/2 & \sqrt{\frac{3}{7}} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad (62)$$

with

$$\tan\theta = \sqrt{7}\omega_1/\omega_Q. \quad (63)$$

The similarity with Eq. (37) for $I=1$ is obvious, but the transforming matrix is less symmetric for $I=3/2$ because the matrix elements $(I_x)_{12}$ and $(I_x)_{23}$ are different.

The diagonalized Hamiltonian can be represented as

$$\begin{aligned} \mathcal{H}_{rT} &= \frac{1}{2}(\omega_e - \omega_Q)I_z^{(13)} + \left(\frac{1}{2}\omega_e + \frac{1}{6}\omega_Q\right) \\ &\quad \times (I_z^{(12)} - I_z^{(23)}) - \frac{5}{3}\omega_Q(I_z^{(14)} + I_z^{(24)} + I_z^{(34)}), \end{aligned} \quad (64)$$

$$\omega_e = (\omega_Q^2 + 7\omega_1^2)^{1/2}, \quad (65)$$

with eigenvalues

$$\begin{aligned} (\mathcal{H}_{rT})_{11} &= -\omega_Q + \frac{1}{2}\omega_e, & (\mathcal{H}_{rT})_{22} &= -\omega_Q - \frac{1}{2}\omega_e, \\ (\mathcal{H}_{rT})_{33} &= -\frac{1}{2}\omega_Q, & (\mathcal{H}_{rT})_{44} &= +\frac{5}{2}\omega_Q. \end{aligned} \quad (66)$$

After evolution for a time t under the influence of the Hamiltonian \mathcal{H}_{rT} the system, originally in thermodynamic equilibrium, is described by the density operator

$$\begin{aligned} \rho_T(t) &= b\left\{-\frac{2}{7}\cos^2\theta/2I_z^{(13)} - \frac{2}{7}\sin^2\theta/2I_z^{(23)} - (8\sqrt{3}/7)\cos\theta/2[I_x^{(13)}\cos\frac{1}{2}(\omega_e - \omega_Q)t + I_y^{(13)}\sin\frac{1}{2}(\omega_e - \omega_Q)t] + (8\sqrt{3}/7)\sin\theta/2\right. \\ &\quad \times [I_x^{(23)}\cos\frac{1}{2}(\omega_e + \omega_Q)t - I_y^{(23)}\sin\frac{1}{2}(\omega_e + \omega_Q)t] + \frac{1}{7}\sin\theta[I_x^{(12)}\cos\omega_e t + I_y^{(12)}\sin\omega_e t] + [I_x^{(14)} + I_x^{(24)} + I_x^{(34)}]\} \end{aligned} \quad (67)$$

For the double quantum expectation value $\langle I_y^{(13)} \rangle(t)$ one obtains

$$\langle I_y^{(13)} \rangle(t) = \text{Tr}\{I_y^{(13)}\rho(t)\} = \text{Tr}\{I_{yT}^{(13)}\rho_T(t)\}$$

$$= -b(4\sqrt{3}/7)[\cos^2\theta/2\sin\frac{1}{2}(\omega_e - \omega_Q)t - \sin^2\theta/2\sin\frac{1}{2}(\omega_e + \omega_Q)t]. \quad (68)$$

In the case of a selective double quantum pulse with ω_1

$\ll \omega_Q$ and $\theta \approx 0$ one can again expand $\frac{1}{2}(\omega_e - \omega_Q)$ with the result

$$\langle I_y^{(13)} \rangle(t) \approx -b \frac{4\sqrt{3}}{7} \sin \frac{7}{4} \frac{\omega_1^2}{\omega_Q} t. \quad (69)$$

The close analogy with Eq. (48), where

$$\langle I_y^{(13)} \rangle(t) \approx -b \sin \frac{\omega_1^2}{\omega_Q} t, \quad \text{for } I=1, \quad (70)$$

is obvious. For the double quantum transitions in the $I=3/2$ spin system the effective rf field along the $x^{(13)}$ (or $x^{(24)}$) axis is given by $7\omega_1^2/4\omega_Q$.

B. Excitation of the triple quantum transition

The triple quantum transition (14) coincides, as mentioned before, with the single quantum transition (23). They are simultaneously excited when the irradiation is applied in the center of the spectrum with $\Delta\omega_0=0$.

The Hamiltonian \mathcal{H}_r , Eq. (58), can be diagonalized for $\Delta\omega_0=0$ by means of the orthogonal transformation

$$T = \frac{1}{\sqrt{2}} \begin{pmatrix} \cos\theta_- & -\sin\theta_- & \cos\theta_+ & -\sin\theta_+ \\ \sin\theta_- & \cos\theta_- & \sin\theta_+ & \cos\theta_+ \\ \sin\theta_- & \cos\theta_- & -\sin\theta_+ & -\cos\theta_+ \\ \cos\theta_- & -\sin\theta_- & -\cos\theta_+ & \sin\theta_+ \end{pmatrix}, \quad (71)$$

where

$$\begin{aligned} \tan 2\theta_- &= (\sqrt{3}/2) \omega_1 / (\omega_Q - \omega_1/2), \\ \tan 2\theta_+ &= (\sqrt{3}/2) \omega_1 / (\omega_Q + \omega_1/2). \end{aligned} \quad (72)$$

The four eigenvalues of \mathcal{H}_r are given by

$$\frac{1}{2}\omega_1 + D_-, \quad \frac{1}{2}\omega_1 - D_-, \quad -\frac{1}{2}\omega_1 + D_+, \quad -\frac{1}{2}\omega_1 - D_+, \quad (73)$$

with

$$\begin{aligned} D_- &= (\omega_Q^2 - \omega_Q \omega_1 + \omega_1^2)^{1/2}, \\ D_+ &= (\omega_Q^2 + \omega_Q \omega_1 + \omega_1^2)^{1/2}. \end{aligned} \quad (74)$$

The time development is then calculated in the eigenbase, and expectation values for the observable magnetization components are computed. Using $\theta_- \approx 0$ and $\theta_+ \approx 0$ for selective irradiation in the center, and expanding the square roots D_- and D_+ in powers of ω_1/ω_Q , one obtains for the single quantum transitions the simple result

$$\begin{aligned} \langle \sqrt{3} I_y^{(12)} \rangle(t) &\approx 0, \\ \langle 2 I_y^{(23)} \rangle(t) &\approx -b \sin 2\omega_1 t, \\ \langle \sqrt{3} I_y^{(34)} \rangle(t) &\approx 0. \end{aligned} \quad (75)$$

The effective rf field along the $x^{(23)}$ axis is thus $2\omega_1$ (correct up to second order in ω_1/ω_Q), where the factor 2 stems from the corresponding matrix element of I_x .

For the triple quantum expectation value one finds

$$\langle I_y^{(14)} \rangle(t) \approx -\frac{3}{2} b \sin^3 \left(\frac{\omega_1^3}{\omega_Q^2} t \right), \quad (76)$$

correct up to third order in ω_1/ω_Q . The rf field strength for exciting the triple quantum transition is thus given by $\frac{3}{8}(\omega_1^2/\omega_Q^2)\omega_1$. It is interesting to compare the effi-

ciency reduction factor $\frac{3}{8}(\omega_1^2/\omega_Q^2)$ with the corresponding factor for the double quantum transitions $\frac{7}{4}(\omega_1/\omega_Q)$. This is in qualitative agreement with the findings of Yatsiv,² who showed that the triple quantum absorption signal is proportional to the third power of the rf field strength.

V. DOUBLE QUANTUM TRANSITION IN THE AB SPIN 1/2 SYSTEM

Single transition operators are also well suited for the description of multiple quantum processes in systems composed of several coupled spins 1/2. These applications to high resolution NMR in liquids will be discussed more thoroughly at another place. The excitation of the double quantum transition in the strongly coupled AB spin system, where A and B are $I=1/2$ nuclei, is shown here as a simple illustrative example.

For irradiation in the center of the spectrum $\omega_r = (\omega_A + \omega_B)/2$ the Hamiltonian is given by

$$\begin{aligned} \mathcal{H}_r &= \mathcal{H}_0 + V, \\ \mathcal{H}_0 &= \frac{1}{2} \Delta\omega (I_{Ax} - I_{Bx}) + 2\pi J I_A \cdot I_B, \\ V &= \omega_1 (I_{Ax} + I_{Bx}), \\ \Delta\omega &= \omega_A - \omega_B. \end{aligned} \quad (77)$$

ω_A and ω_B are the Larmor frequencies of the two nuclei and J is the scalar coupling constant. An analytical diagonalization of \mathcal{H}_r is not feasible in this case. Therefore, an expansion of the time evolution operator is used^{13,14}:

$$\begin{aligned} \exp(-i\mathcal{H}_r t) &= \left\{ T \exp \left[-i \int_0^t V(t') dt' \right] \right\} \exp(-i\mathcal{H}_0 t) \\ &= \exp \left\{ -i [\bar{V}(t) + \bar{V}^{(1)}(t) + \dots] t \right\} \exp(-i\mathcal{H}_0 t), \end{aligned} \quad (78)$$

with

$$\bar{V}(t') = \exp(-i\mathcal{H}_0 t') V \exp(+i\mathcal{H}_0 t'). \quad (79)$$

T is here the time ordering operator.¹⁴

For a selective double quantum pulse which does not perturb the inner lines of the AB spectrum, i.e.,

$$\omega_1 \ll \left(\frac{\Omega}{2} - \pi J \right), \quad \left(\frac{\Omega}{2} - \pi J \right) t \gg 1, \quad (80)$$

where

$$\Omega = [\Delta\omega^2 + (2\pi J)^2]^{1/2}, \quad (81)$$

a calculation in the eigenbase of \mathcal{H}_0 (with eigenstates ordered according to decreasing magnetic quantum number) leads to the result

$$\bar{V}(t) = 0, \quad (82)$$

$$\begin{aligned} \bar{V}^{(1)}(t) &= -(\omega_1^2/\Delta\omega^2) \{ 8\pi J (I_x^{(14)} \\ &\quad + I_x^{(12)} - I_x^{(24)}) - 2[\Omega + (2\pi J)^2/\Omega] I_x^{(23)} \}. \end{aligned} \quad (83)$$

The action of this pulse on a spin system in thermodynamic equilibrium

$$\rho(0) = bI_x = 2bI_x^{(14)} \quad (84)$$

is described by the simple result

$$\rho(t) = 2b \{ I_x^{(14)} \cos \zeta t + I_y^{(14)} \sin \zeta t \}, \quad (85)$$

where

$$\zeta = (\omega_1^2 / \Delta\omega^2) 8\pi J = \frac{2\pi J}{\Delta\omega/2} \frac{\omega_1}{\Delta\omega/2} \omega_1. \quad (86)$$

The effective rf field ζ points along the negative $x^{(14)}$ axis. Compared to the field ω_1 , which would determine the flip angle for single quantum transitions, ζ is smaller by a factor of $\omega_1/(\Delta\omega/2)$, in complete analogy with the factor ω_1/ω_Q for a single spin $I=1$, Eq. (48). The second factor $2\pi J/(\Delta\omega/2)$, multiplying ω_1 in Eq. (86), is an expression of the fact that, without internuclear coupling, no double quantum transition can be induced for spins $I=1/2$.

At first sight it seems that the larger the chemical shift difference $\Delta\omega$ the easier it becomes to selectively excite the double quantum transition since, in Eq. (80), (i) $(\Omega/2 - \pi J)$ increases and (ii) a longer pulse duration t is required to rotate the (14) magnetization through a given flip angle α , due to the smaller effective rf field strength ζ , Eq. (86). However, relaxation has not been taken into account in these considerations, which will set an upper limit to useful pulse lengths t .

VI. CONCLUSIONS

A limited number of particularly simple applications of single transition operators has been described in this paper. They served the purpose to demonstrate the "natural" choice of the operators defined in Sec. II. Applications to more complicated situations can easily be conceived, particularly in connection with selective double resonance experiments and also in two-dimensional spectroscopy.¹⁵ Some examples will be treated in another place.

It is also possible to generalize the concept of a single transition operator to the notion of a multiple transition operator designed for situations where a number of selected transitions, e.g., degenerate transitions, is simultaneously excited and/or observed.

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