

SPIN DIFFUSION BETWEEN INEQUIVALENT QUADRUPOLAR NUCLEI BY DOUBLE-QUANTUM FLIP-FLOPS

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A new mechanism for spin diffusion between quadrupolar nuclei whose NMR lines do not overlap is proposed. For spin-1 nuclei, double-quantum flip-flop transitions allow the diffusion of Zeeman order, but not quadrupolar order, without requiring an extraneous energy reservoir. The flip-flop rate is sensitive to the relative signs of the quadrupolar splittings.

1. Introduction

Spin diffusion in NMR typically occurs by mutual spin flip-flop transitions between coupled nuclei whose individual resonance lines overlap. Such a flip-flop transition is depicted in fig. 1a. The rate W at which flip-flop transitions occur for a pair of nuclei, called the cross relaxation rate, is roughly $W \approx d^2\delta^{-1}$, where d is the coupling strength and δ is the linewidth [1]. When the resonance lines do not overlap, spin diffusion is expected to be strongly quenched since the flip-flop transitions no longer conserve energy [2], as in fig. 1b. Some residual spin diffusion may remain in the presence of a dipolar reservoir capable of absorbing small energy differences [3,4].

Recent studies indicate that spin diffusion between inequivalent spin-1 nuclei in solids is not entirely quenched even in the case where the difference between quadrupole splittings exceeds the resonance linewidths, i.e. in the case where the lines do not overlap [5–7]. Suter and Ernst [7] have presented data indicating that the cross relaxation rate between pairs of ^{14}N nuclei in such a case is proportional to $\Delta\Omega^{-2}$, where $\Delta\Omega$ is the line separation. Two explanations for the presence of the residual spin diffusion have been advanced. Schajor et al. [6] suggest a multiple spin flip-flop as the basic diffusion step, but give no quantitative details. Suter and Ernst [7] treat each spin-1 nucleus as a pair of independent, mismatched spin-1/2 particles which are in turn coupled to a proton dipolar re-

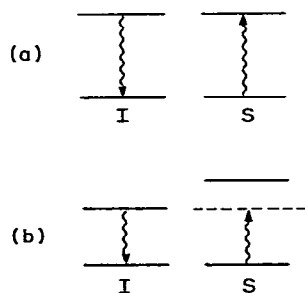


Fig. 1. Flip-flop transitions for a pair of coupled spin-1/2 nuclei. (a) The I and S resonance lines overlap, so that the single-quantum ($\Delta m = \pm 1$) flip-flop conserves energy. (b) The I and S resonance lines do not overlap, requiring an extraneous energy reservoir to absorb the energy change in the single-quantum flip-flop.

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servoir. Based on the general theory of Demco et al. [8], they derive a theoretical expression for the cross relaxation rate which reduces to $W \approx d^2 \Delta \Omega^{-2}$ in the limit $d^2 \ll \Delta \Omega^2 \ll M_{2I}$, where M_{2I} is the second moment of the proton-proton dipole interactions.

In this letter we elaborate on an alternative suggestion that double-quantum ($\Delta m = 2$) transitions may be important in spin-1 spin diffusion [9], and point out how a double-quantum mechanism leads to a similar inverse quadratic dependence for the cross relaxation rate without invoking any couplings other than those between the spin-1 nuclei themselves.

2. Double-quantum flip-flops

The essential idea behind the double-quantum mechanism is illustrated in fig. 2. Consider two coupled spin-1 nuclei I and S with identical Larmor frequencies and with quadrupole splittings ω_I and ω_S . If $|\omega_I| = |\omega_S|$ as in figs. 2a and 2b, energy-conserving flip-flop transitions may occur in which the spin quantum number of each nucleus changes by ± 1 . If $|\omega_I| \neq |\omega_S|$ as in figs. 2c and 2d, the same transitions no longer conserve energy, but transitions in which the spin quantum number of each nucleus changes by ± 2 do conserve energy. In other words, although the resonance lines in the single-quantum spectrum of the two nuclei may not overlap, the double-quantum spectrum will consist of two overlapping lines. An approximate expression for the rate of double-quantum flip-flop transitions can be derived with second order perturbation theory, treating the I - S coupling as a perturbation, as in the explanation of double-quantum decoupling given by Pines et al. [10]. The result is:

$$W = 2\pi [d^4 / (\omega_I + \omega_S)^2] f(0),$$

where $f(0)$ is the overlap integral of the double-quantum lines.

Two predictions following from the double-quantum spin diffusion mechanism deserve emphasis:

(1) The single-quantum spectrum of the I - S system depends only on $|\omega_I|$ and $|\omega_S|$, while the cross relaxation rate is sensitive to the relative signs of ω_I and ω_S . This point can be understood by comparing figs. 2c and 2d. The virtual, or intermediate, state in fig. 2d, where ω_I and ω_S are of opposite sign, is more nearly resonant with the initial and final states than in fig. 2c. Double-quantum spin diffusion is therefore expected to be more efficient when ω_I and ω_S are of opposite sign. It is only in that case that $(\omega_I + \omega_S)^2 = \Delta \Omega^2$.

(2) Double-quantum flip-flops provide a pathway for the diffusion of Zeeman, but not quadrupolar, spin order. Zeeman order corresponds to a population difference between the $m = 1$ and $m = -1$ levels of a spin-1 nucleus, while quadrupolar order corresponds to a population difference between the $m = 0$ and the $m = \pm 1$ levels. Double-

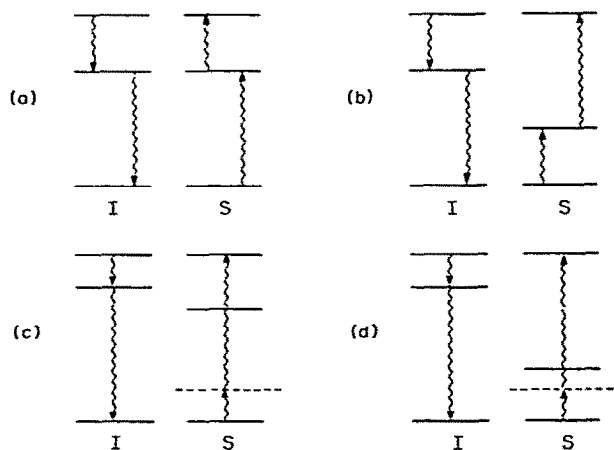


Fig. 2. Flip-flop transitions for a pair of coupled spin-1 nuclei with quadrupole splittings ω_I and ω_S . (a) $\omega_I = \omega_S$. (b) $\omega_I = -\omega_S$. Single-quantum flip-flops conserve energy in both cases. (c) $|\omega_I| \neq |\omega_S|$; ω_I and ω_S are both negative. (d) $|\omega_I| \neq |\omega_S|$; ω_I is negative and ω_S is positive. The double-quantum flip-flop conserves energy in both cases, even though the resonance lines do not overlap. Case (d) leads to a greater flip-flop rate, since the intermediate state is nearly resonant.

quantum flip-flops will tend to equalize the population differences between the $m = 1$ and $m = -1$ levels of I and S . If there is quadrupolar order at spin I and no order at spin S , i.e. all three levels of spin S are equally populated, double-quantum flip-flops will be ineffective in transferring the quadrupolar order to spin S , since the population difference between the $m = 1$ and $m = -1$ levels is already zero for both I and S .

3. Operator theory

A more formal insight into the mechanisms of spin diffusion between spin-1 nuclei can be attained with average hamiltonian theory [11]. Neglecting chemical shifts, the high-field, rotating-frame hamiltonian for the I - S system is

$$\mathcal{H} = \mathcal{H}_Q + \mathcal{H}_d, \quad \mathcal{H}_Q = \omega_I(I_z^2 - \frac{1}{2}I^2) + \omega_S(S_z^2 - \frac{1}{3}S^2), \quad \mathcal{H}_d = d(3I_zS_z - I \cdot S),$$

$$d = (\gamma_I\gamma_S/2r^3)(1 - 3 \cos^2\theta_{IS}).$$

In an interaction representation with respect to \mathcal{H}_Q , the hamiltonian becomes

$$\mathcal{H}_d(t) = \exp(i\mathcal{H}_Q t) \mathcal{H}_d \exp(-i\mathcal{H}_Q t).$$

Provided that $\mathcal{H}_d(t)$ is periodic in time, we can use average hamiltonian theory to define an equivalent constant hamiltonian in the interaction representation. Using the fictitious spin-1/2 operators defined by Vega [12] and by Wokaun and Ernst [13]:

$$\begin{aligned} \mathcal{H}_d(t) = & 2d[4I_z^{1-3}S_z^{1-3} - \cos(\alpha t)(I_x^{1-2}S_x^{1-2} + I_y^{1-2}S_y^{1-2} + I_x^{2-3}S_x^{2-3} + I_y^{2-3}S_y^{2-3}) \\ & - \sin(\alpha t)(I_x^{1-2}S_y^{1-2} - I_y^{1-2}S_x^{1-2} - I_x^{2-3}S_y^{2-3} + I_y^{2-3}S_x^{2-3}) \\ & - \cos(\beta t)(I_x^{1-2}S_x^{2-3} + I_y^{1-2}S_y^{2-3} + I_x^{2-3}S_x^{1-2} + I_y^{2-3}S_y^{1-2}) \\ & - \sin(\beta t)(I_x^{1-2}S_y^{2-3} - I_y^{1-2}S_x^{2-3} - I_x^{2-3}S_y^{1-2} + I_y^{2-3}S_x^{1-2})]. \end{aligned}$$

Here $\alpha = \omega_I - \omega_S$ and $\beta = \omega_I + \omega_S$. If $\alpha = 0$, $\mathcal{H}_d(t)$ becomes periodic with period $\tau = 2\pi\beta^{-1}$. The average hamiltonian is then:

$$\mathcal{H}_d^{(0)} = 2d(4I_z^{1-3}S_z^{1-3} - I_x^{1-2}S_x^{1-2} - I_y^{1-2}S_y^{1-2} - I_x^{2-3}S_x^{2-3} - I_y^{2-3}S_y^{2-3}).$$

$\mathcal{H}_d^{(0)}$ can induce first-order transitions such as those pictured in fig. 2a. Similarly, if $\beta = 0$:

$$\mathcal{H}_d^{(0)} = 2d(4I_z^{1-3}S_z^{1-3} - I_x^{1-2}S_x^{2-3} - I_y^{1-2}S_y^{2-3} - I_x^{2-3}S_x^{1-2} - I_y^{2-3}S_y^{1-2}).$$

Here $\mathcal{H}_d^{(0)}$ can induce first-order transitions such as those pictured in fig. 2b.

The novel component of this letter is the case where neither α nor β is zero. In this case the average hamiltonian is diagonal and it is necessary to calculate a first-order correction term [11] in order to discover the source of the residual spin diffusion. Suppose $|\alpha| > |\beta|$. If we define $\pi = 2n\pi\beta^{-1}$, for some integer n subject to the restriction $\tau \ll d^{-1}$, $\mathcal{H}_d(t)$ is periodic with a period τ as long as $\alpha = \beta kn^{-1}$ for some integer k . In a real system, α may differ slightly from this value, but such a slight difference should not alter the physical situation appreciably provided that $|\beta| \gg d$. A similar argument holds for the case $|\beta| > |\alpha|$. Having thus defined a period, we can approximate the average hamiltonian expansion by its first two terms:

$$\tilde{\mathcal{H}}_d \approx \mathcal{H}_d^{(0)} + \mathcal{H}_d^{(1)} = A + B + C,$$

where

$$\begin{aligned}
 A &= 8d I_z^{1-3} S_z^{1-3} - \frac{2}{3}(d^2/\alpha)(I_z^{2-3} - S_z^{2-3} - I_z^{1-2} + S_z^{1-2}) \\
 &\quad - \frac{4}{9}(d^2/\beta)(2I_z^{2-3} S_z^{2-3} - I_z^{2-3} S_z^{1-2} - I_z^{1-2} S_z^{2-3} + 2I_z^{1-2} S_z^{1-2}) \\
 &\quad + I_z^{1-2} S_z^{1-3} + 2I_z^{1-3} S_z^{1-3} + I_z^{1-3} S_z^{2-3} + I_z^{1-3} S_z^{1-2} + I_z^{2-3} S_z^{1-3} + \frac{3}{2}I_z^{2-3} - \frac{3}{2}I_z^{1-2} + \frac{3}{2}S_z^{2-3} - \frac{3}{2}S_z^{1-2}), \\
 B &= (4d^2/\beta)(I_x^{1-2} S_x^{2-3} + I_y^{1-2} S_y^{2-3} + I_x^{2-3} S_x^{1-2} + I_y^{2-3} S_y^{1-2}), \\
 C &= (2d^2/\beta)(I_x^{1-3} S_x^{1-3} + I_y^{1-3} S_y^{1-3}).
 \end{aligned}$$

Term A is diagonal in the basis of eigenstates of \mathcal{H}_Q . Term B would give single-quantum flip-flop transitions in a first-order perturbation theory treatment if it were not for the fact that energy conservation would be violated in the absence of an external energy reservoir. Term C is responsible for double-quantum flip-flop transitions in a first order treatment. Note that the double-quantum transition rate calculated in first order using $\tilde{\mathcal{H}}_d$ as the perturbation is the same as the rate calculated in second order using \mathcal{H}_d as the perturbation [eq. (1)].

4. Computer simulations

An experimental measurement of cross relaxation in the two-spin system described above may begin with the creation of a non-equilibrium density matrix proportional to $(I_z + S_z) - \frac{1}{2}I_z + \frac{1}{2}(3I_z^2 - I^2)$, by the application of a selective π pulse to one of the I spin transitions. The $I_z + S_z$ part will remain unchanged under the action of \mathcal{H} . The I_z and $3I_z^2 - I^2$ parts represent Zeeman and quadrupolar order, respectively, at spin I . The Zeeman and quadrupolar order at spin I may subsequently evolve independently into Zeeman and quadrupolar order at spin S . No conversion of Zeeman order to quadrupolar order may be expected, due to their different symmetry properties.

The results of computer simulations of the transfer of Zeeman order are shown in fig. 3. We calculated the amplitudes $P_z(t)$ and $\tilde{P}_z(t)$ that an initial density matrix $\rho(0) = I_z$ will develop into $\rho(t) = S_z$ under \mathcal{H} and $\tilde{\mathcal{H}}_d$, respectively:

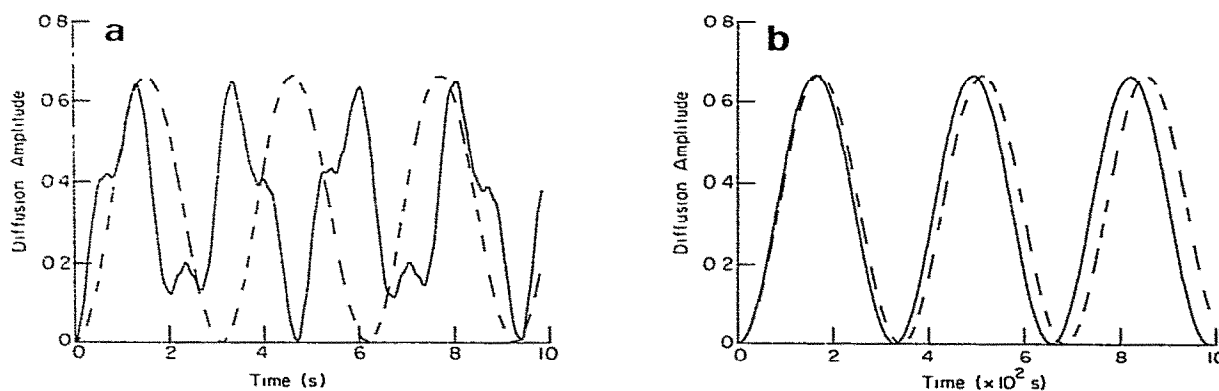


Fig. 3. Theoretical amplitudes of the diffusion of Zeeman order between a pair of coupled spin-1 nuclei with quadrupole splittings ω_I and ω_S and dipole coupling constant d (rad/s). The results of exact (solid line) and approximate, average hamiltonian theory (dotted line) calculations are shown. (a) $\omega_I = 20$, $\omega_S = -10$, $d = 3$. (b) $\omega_I = 20$, $\omega_S = -10$, $d = 0.3$. The agreement between the exact and approximate calculations is good when the ratio of $|d|$ to $|\omega_I + \omega_S|$ is less than 0.05.

$$P_z(t) = \text{Tr}[S_z \exp(-i\mathcal{H}t) I_z \exp(i\mathcal{H}t)] / \text{Tr}(S_z^2).$$

$$\begin{aligned} \tilde{P}_z(t) &= \text{Tr}[S_z \exp(-i\mathcal{H}_Q t) (-i\tilde{\mathcal{H}}_d t) I_z \exp(i\tilde{\mathcal{H}}_d t) \exp(i\mathcal{H}_Q t)] / \text{Tr}(S_z^2) \\ &= \text{Tr}[S_z \exp(-i\tilde{\mathcal{H}}_d t) I_z \exp(i\tilde{\mathcal{H}}_d t)] / \text{Tr}(S_z^2). \end{aligned}$$

Good quantitative agreement between $\tilde{P}_z(t)$ and $P_z(t)$ was found when the ratio of $|d|$ to $|\omega_I + \omega_S|$ was less than 0.05. In such cases, the diffusion amplitude depended only on $\omega_I + \omega_S$ for a given d , as anticipated by the double-quantum mechanism. The maxima of 0.67 in $\tilde{P}_z(t)$ indicate the efficiency of double-quantum flip-flops in transferring Zeeman order.

As calculated above for a single pair of isolated spin-1 nuclei, $\tilde{P}_z(t)$ is an oscillatory function. However, in a real sample in which the resonance lines are broadened, for example by unresolved spin-spin couplings or by orientational inhomogeneities, cross relaxation will proceed from one nucleus to another at a time-independent rate, provided that the linewidths are large compared to the frequency of oscillation of $\tilde{P}_z(t)$. If that frequency is ν (Hz), the expected rate will be $W = 2\pi^3\nu^2 f(0)$.

The agreement between the first-order $\tilde{P}_z(t)$ and the exact $P_z(t)$ calculations indicates that the residual spin diffusion among inequivalent spin-1 nuclei can be interpreted as the result of a first-order correction term, in the sense of average hamiltonian theory, in a system with no other degrees of freedom. It should be stressed that neither calculation includes the presence of an energy reservoir such as coupled spins of a different type. If an energy reservoir is present, single-quantum flip-flop terms contained in the zeroth-order average hamiltonian may dominate the spin diffusion process.

We also calculated the amplitudes $P_Q(t)$ and $\tilde{P}_Q(t)$ that an initial density matrix $\rho(0) = 3I_z^2 - I^2$ would evolve into $\rho(t) = 3S_z^2 - S^2$ under \mathcal{H} and $\tilde{\mathcal{H}}_d$. There the agreement was not quantitative. The maxima of $P_Q(t)$ were larger than those of $\tilde{P}_Q(t)$, suggesting that the use of \mathcal{H}_d results in an underestimation of the efficiency of single-quantum flip-flops that allow the diffusion of quadrupolar order. Even so, the maxima of $P_Q(t)$ were small. As an example, for $\omega_I = 20$, $\omega_S = -10$ and $d = 0.5$, the maxima of $P_Q(t)$ were ≈ 0.012 .

5. Conclusion

In general, several mechanisms may contribute to spin diffusion between inequivalent spin-1 nuclei, including off-resonance single-quantum flip-flops. The importance of the double-quantum mechanism presented here may be assessed experimentally by examining the dependence of the cross relaxation rate on the relative signs of the quadrupole splittings, by decoupling the nuclei of interest from possible energy reservoirs in the form of other nuclear spins and by studying the diffusion of both Zeeman and quadrupolar order. Clearly these considerations can be extended to quadrupolar nuclei with $I > 1$.

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