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J-Stabilization of singlet states in the solution NMR of multiple-spin systems

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Abstract

Long-lived singlet states have been observed in the solution NMR of spin systems containing more than two coupled spins, despite the fact that the singlet state is expected to be quenched by small long-range J-couplings. We show that the stability of localized singlet states may be explained by taking into account the intra-pair J-coupling between the two spins which participate in the singlet state. The relatively strong intra-pair J-coupling protects the singlet state against quenching by weaker out-of-pair J-couplings.

Keywords: Relaxation; Long-lived spin states; Singlet states

1. Introduction

Singlet states with much longer lifetimes than T_1 may exist in systems containing isolated pairs of coupled spins-1/2 [1–6]. The long lifetimes of these states are revealed if singlet-triplet interconversion is suppressed, either by transporting the sample into a region of low magnetic field [1,2], or by using resonant radiofrequency irradiation in high magnetic field [3–6]. Singlet lifetimes of up to $37T_1$ have been demonstrated [6]. The long lifetimes of these states have been exploited for studies of spatial diffusion [4] and chemical exchange [6]. Long-lived spin states are expected to be useful for transporting hyperpolarized nuclear spin order, such as that prepared by techniques such as dynamic nuclear polarization (DNP) [7] or by chemical reactions of parahydrogen [8–12,10,13–15].

The existence of long-lived spin states has also been demonstrated in systems of more than two coupled spins-1/2 [15,16], including large biomolecules [6]. However, the precise nature of the long-lived states in multiple-spin systems is not yet clear. The most obvious interpretation is that one spin pair combines to form a singlet state, with the other spins being passive. This *localized singlet state* does not relax under the motional modulation of the *intra*-pair dipole–dipole coupling, and is therefore relatively long-lived.

The localized singlet hypothesis is challenged by the existence of finite J-couplings between the spins that participate in the singlet state and other nuclei. In general, these *out-of-pair J-couplings* do not commute with the singlet population operator. The out-of-pair J-couplings are therefore expected to transform the singlet population into other density matrix elements, which are in general short-lived. This mechanism is therefore expected to quench the singlet state on a timescale given approximately by the inverse of the out-of-pair J-couplings [16]. However, this theoretical expectation is not consistent with experimental observations of several $AA'BB'$ and $AA'XX'$ spin systems [16]. This discrepancy suggests that either (i) the long-lived states in these systems are not localized singlets, or (ii) a mechanism exists which protects the localized singlets against the out-of-pair J-couplings.

In this communication, we use numerical analysis of the propagation superoperator to demonstrate the existence of a stabilization mechanism for localized singlet states, which we call J-stabilization. A sufficiently large J-coupling *within* the spin pair suppresses the influence of out-of-pair J-cou-

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plings. A localized singlet state involving spins with a large mutual J-coupling is protected against J-couplings to spins outside the pair as well as the intra-pair dipole–dipole relaxation mechanism. The localized singlet does, however, still relax under motional modulation of the out-of-pair dipole–dipole couplings.

2. Liouvillian eigenvalue analysis

The equation of motion of the spin density operator, in the presence of simultaneous coherent and incoherent interactions, is given by

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho(t) = \hat{\mathcal{L}}\rho(t) \tag{1}$$

where the Liouvillian superoperator is

$$\hat{\mathcal{L}} = -\mathrm{i}\hat{\mathcal{H}} + \hat{\Gamma} \tag{2}$$

Here $\hat{\mathcal{H}}$ is the superoperator for commutation with the coherent Hamiltonian $\mathcal{H}$, and $\hat{\Gamma}$ is the relaxation superoperator, generated by fluctuations of the incoherent Hamiltonian.

The Liouvillian superoperator $\hat{\mathcal{L}}$ may be expressed as a $\mathcal{N}^2 \times \mathcal{N}^2$ matrix in Liouville space [17], where $\mathcal{N}$ is the number of spin states (equal to 2^N for the case of N coupled spins-1/2). The superoperator $\hat{\mathcal{L}}$ has $\mathcal{N}^2$ eigenvalue-eigenoperator pairs $\{L_q, Q_q\}$, with $q \in \{0 \ldots \mathcal{N}^2 - 1\}$:

$$\hat{\mathcal{L}}Q_q = L_q Q_q \tag{3}$$

The eigenvalues L_q are complex in general, with negative real parts, and may be expressed:

$$L_q = -\lambda_q + \mathrm{i}\omega_q \tag{4}$$

where λ_q and ω_q are real. Eigenoperators Q_q which have complex eigenvalues ($\omega_q \neq 0$) correspond to coherences, which oscillate at the frequency ω_q and decay with a rate constant λ_q. Eigenoperators which have real eigenvalues ($\omega_q = 0$) correspond to combinations of spin state populations, which are conserved under evolution. The decay constants λ_q correspond to the decay rate constants of these stable population configurations.

In the following discussion, we assume that all eigenoperators are normalized, i.e. $(Q_q|Q_{q'}) = \delta_{qq'}$, where the operator bracket is defined [17]

$$(A|B) = \mathrm{Tr}\{A^\dagger B\} \tag{5}$$

The Liouvillian superoperator always has one vanishing eigenvalue $L_0 = 0$: the corresponding eigenvector is proportional to the sum of all population operators:

$$Q_0 = \mathcal{N}^{-1/2} \sum_{r=1}^{\mathcal{N}} |r\rangle\langle r| \tag{6}$$

The sum of all populations is always conserved for a closed spin system.

The remaining rate constants λ_q, with $q \in \{1 \ldots \mathcal{N}^2 - 1\}$, comprise the set of decay rate constants for all conserved configurations of populations and coherences. A particularly small value of $\lambda_{q>0}$ indicates the presence of a long-lived mode of nuclear spin order.

The nature and existence of long-lived states in arbitrarily complex spin systems may therefore be explored by (i) setting up the superoperators $\hat{\mathcal{H}}$ and $\hat{\Gamma}$, assuming a particular spin system, set of coherent interactions, and relaxation model; (ii) numerical diagonalization of the $\mathcal{N}^2 \times \mathcal{N}^2$ matrix representation of $\hat{\mathcal{L}}$; (iii) identification of eigenvalues with particularly small real parts (ignoring the zero eigenvalue); (iv) examination of the eigenoperator(s) corresponding to the small real eigenvalue(s).

The technique is illustrated in Fig. 1, which corresponds to an ensemble of inequivalent spin-1/2 pairs, in the presence of a resonant radiofrequency field at the mean of the two chemical shift frequencies. Since each spin-1/2 pair has 4 spin states, there are $4^2 = 16$ Liouvillian eigenvalues.

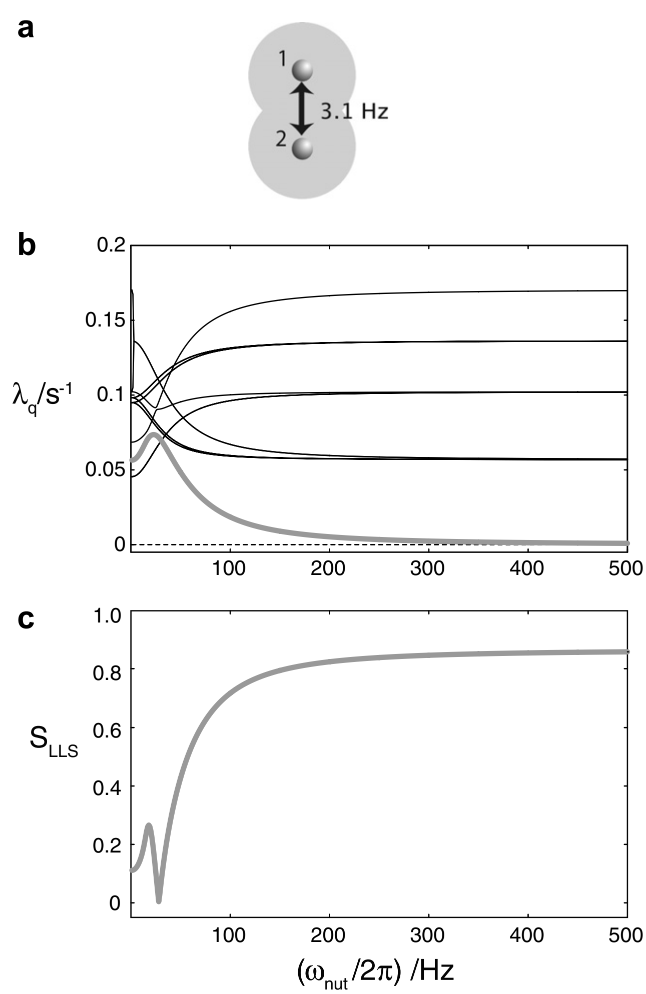

Fig. 1. (a) Two-spin system used in the simulation. The simulation parameters are: chemical shift frequency difference = 76.0 Hz; J-coupling = 3.1 Hz; dipole–dipole coupling = −18.5 kHz; rotational correlation time = 8.4 ps. (b) Decay rate constants of the Liouvillian eigenoperators, as a function of the rf field amplitude, expressed as a nutation frequency ω_{nut}. The long-lived eigenoperator is shown by the bold grey line. The dashed line indicates the conserved sum of all populations. (c) Singlet content of the long-lived eigenoperator, as a function of the nutation frequency ω_{nut}.

The 16 complex eigenvalues were determined as a function of the nutation frequency ω_{nut}, which is a measure of the rf field amplitude. Fig. 1b shows the variation in the decay rate constants λ_q (given by minus the real parts of the Liouvillian eigenvalues) as a function of the nutation frequency. The imaginary parts of the eigenvalues are not shown.

Fig. 1b shows how the decay rate constants λ_q vary as a function of the rf nutation frequency ω_{nut}. As described above, there is always one zero eigenvalue at all rf field values, which corresponds to the conserved sum of all spin state populations (dotted line in Fig. 1b). The real parts of the other 15 eigenvalues vary with the applied rf field. When the nutation frequency increases beyond around 60 Hz, one eigenvalue separates from the pack and drops towards zero (bold grey line in Fig. 1b). This small eigenvalue indicates the long-lived spin state. A sufficiently large rf field suppresses the chemical shift difference, in the sense of average Hamiltonian theory, and allows the long-lived singlet to become manifest.

Suppose that the eigenvalue-eigenoperator pair corresponding to the long-lived mode of spin order is labelled $\{\lambda_{\text{LLS}}, Q_{\text{LLS}}\}$. The nature of the long-lived state may be explored by evaluating its *singlet content*, which is defined as follows:

$$S_{\text{LLS}} = (P(S_0)|Q_{\text{LLS}}) \tag{7}$$

where the population operator of the singlet state is given by

$$P(S_0) = |S_0\rangle\langle S_0| \tag{8}$$

and the singlet and triplet kets for the spin pair are given by:

$$\begin{aligned}
|S_0\rangle &= \tfrac{1}{\sqrt{2}}(|\alpha\beta\rangle - |\beta\alpha\rangle)\\
|T_{+1}\rangle &= |\alpha\alpha\rangle\\
|T_0\rangle &= \tfrac{1}{\sqrt{2}}(|\alpha\beta\rangle + |\beta\alpha\rangle)\\
|T_{-1}\rangle &= |\beta\beta\rangle
\end{aligned} \tag{9}$$

For the two-spin case, the singlet content is given by the following matrix element of the eigenoperator:

$$S_{\text{LLS}} = \langle S_0|Q_{\text{LLS}}|S_0\rangle \tag{10}$$

The singlet content S_{LLS} of the long-lived eigenoperator Q_{LLS} is plotted as a function of nutation frequency in Fig. 1c. As expected, the singlet content increases as the nutation frequency increases. In the limit of large ω_{nut}, the singlet content of the long-lived state tends to the value $\frac{1}{2}\sqrt{3} \cong 0.866$.

At first sight, it is surprising that the singlet content does not tend to unity at large values of ω_{nut}. However, we must remember that the sum of all populations is also an eigenoperator, and that the Liouvillian eigenoperators are very close to being orthogonal, since the commutation superoperator of the Hamiltonian is hermitian, and has orthogonal eigenoperators. The long-lived eigenoperator Q_{LLS} is therefore almost orthogonal to the eigenoperator Q_0, which represents the conserved sum of all populations (Eq. (6)). The eigenoperator Q_{LLS} therefore tends to the following expression in the limit of large ω_{nut}:

$$Q_{\text{LLS}} \to \tfrac{1}{2}\sqrt{3}\{|S_0\rangle\langle S_0| - \tfrac{1}{3}(|T_{+1}\rangle\langle T_{+1}| + |T_0\rangle\langle T_0| + |T_{-1}\rangle\langle T_{-1}|)\} \tag{11}$$

The numerical factors ensure that Q_{LLS} is normalized and orthogonal to Q_0. Strictly speaking, the long-lived mode of nuclear spin order is not given by the singlet population alone, but by the singlet population minus the mean of the triplet state populations.

3. *J*-stabilization of singlet states

Liouvillian eigenvalue analysis may be used to investigate the nature of long-lived states in higher spin systems, in particular their persistence in the presence of long-range *J*-couplings.

The simulations shown in Fig. 2 illustrate the phenomenon of *J*-stabilization. A third spin is coupled to the two-

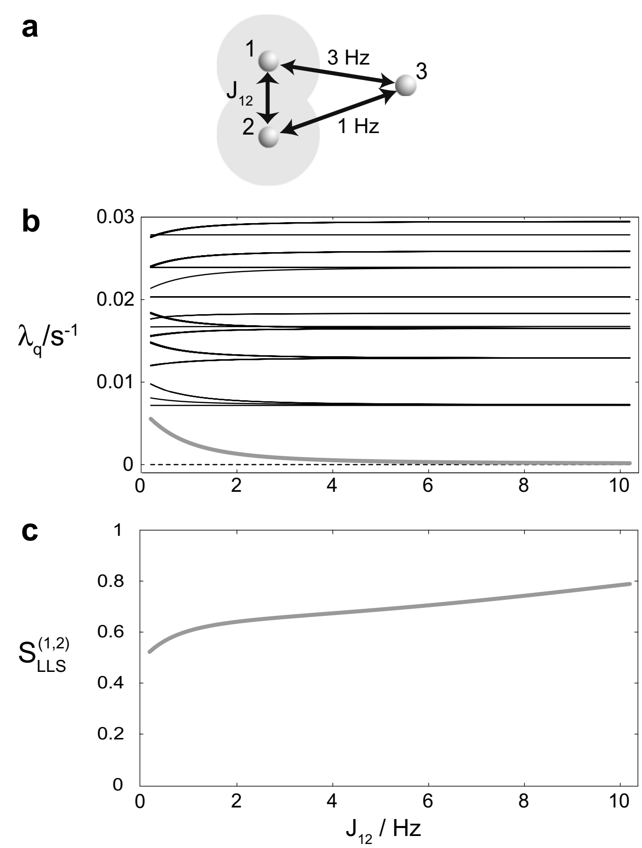

Fig. 2. (a) Three-proton system used in the simulation. The simulation parameters are as follows: isotropic chemical shift frequencies, relative to the rf carrier frequency: $\omega_1/2\pi = -200$ Hz, $\omega_2/2\pi = +200$ Hz, and $\omega_3/2\pi = +2$ kHz; *J*-couplings $J_{13} = 3$ Hz and $J_{23} = 1$ Hz; Rf nutation frequency $\omega_{\text{nut}}/2\pi = 3.5$ kHz; Dipole–dipole couplings $b_{12}/2\pi = -7.8$ kHz, $b_{13} = 0$, $b_{23} = 0$. Rotational correlation time $\tau_c = 7.5$ ps. Spin I_3 experiences an external random field of magnitude $B_{\text{ERF}} = 66$ μT with a correlation time $\tau_{\text{ERF}} = 23$ ps. (b) Decay rate constants of the Liouvillian eigenoperators, as a function of the intra-pair *J*-coupling J_{12}. The long-lived eigenoperator is shown by the bold grey line. The dashed line indicates the conserved sum of all populations. (c) Singlet content of the long-lived eigenoperator, as a function of the intra-pair *J*-coupling J_{12}.

spin system, using two different J-couplings. For simplicity, the dipole–dipole interactions involving the third spin are set to zero, in order to isolate the effect of the J-couplings. The simulation includes an rf field with a nutation frequency $\omega_{\text{nut}}/2\pi = 3.5$ kHz, which is sufficient to suppress the chemical shift difference between spins I_1 and I_2.

The issue at stake is whether the small J-couplings to the third spin (J_{13} and J_{23}) quench the long-lived singlet state between the first two spins, which is locked by the relatively strong rf field. In order to isolate this issue, the third spin is given a relatively rapid random field relaxation, to ensure that the only potential long-lived state is associated with the singlet state composed of spins I_1 and I_2.

The decay rate constants, which correspond to minus the real parts of the Liouvillian eigenvalues, are plotted against the intra-pair J-coupling J_{12} in Fig. 2b. There are 64 eigenvalues in all, including the zero eigenvalue corresponding to the conserved sum of all populations, shown by a dotted line. As the value of J_{12} increases, the decay rate constant of the long-lived state, shown by the thick grey line, drops sharply. Fig. 2b demonstrates that (i) no long-lived state exists in the three-spin system if the intra-pair J-coupling J_{12} vanishes; and (ii) A sufficiently large value of J_{12} restores the long-lived state, and protects it against quenching by the out-of-pair J-couplings J_{13} and J_{23}.

Further simulations (not shown) indicate that the important factor is the *difference* in the out of pair J-couplings, $|J_{13} - J_{23}|$. Identical J-couplings J_{13} and J_{23} do not quench the singlet state.

The singlet state involving spins I_1 and I_2 comes in two varieties, dependent on the state of the third spin, which we will denote as follows:

$$\begin{aligned} |S_0^{(1,2)}\alpha^{(3)}\rangle &= 2^{-1/2}(|\alpha\beta\alpha\rangle - |\beta\alpha\alpha\rangle) \\ |S_0^{(1,2)}\beta^{(3)}\rangle &= 2^{-1/2}(|\alpha\beta\beta\rangle - |\beta\alpha\beta\rangle) \end{aligned} \tag{12}$$

The singlet population operator for spins I_1 and I_2, irrespective of the state of spin I_3 is given by

$$P(S_0^{(1,2)}) = |S_0^{(1,2)}\alpha^{(3)}\rangle\langle S_0^{(1,2)}\alpha^{(3)}| + |S_0^{(1,2)}\beta^{(3)}\rangle\langle S_0^{(1,2)}\beta^{(3)}| \tag{13}$$

The corresponding singlet content of a long-lived eigenoperator Q_{LLS} is given by

$$S_{\text{LLS}}^{(1,2)} = (P(S_0^{(1,2)})|Q_{\text{LLS}}) \tag{14}$$

The singlet content $S_{\text{LLS}}^{(1,2)}$ of the long-lived eigenoperator is examined in Fig. 2c. As expected, the singlet content increases as the intra-pair J-coupling becomes larger. However, this time, it approaches the limiting value of $\sqrt{3}/2$ very slowly.

The J-stabilization of singlet states may be understood as a consequence of the secular approximation. Consider a basis composed of the singlet kets in Eq. (12), and the triplet kets defined as follows:

$$\begin{aligned} |T_{+1}^{(1,2)}\alpha^{(3)}\rangle &= |\alpha\alpha\alpha\rangle \\ |T_0^{(1,2)}\alpha^{(3)}\rangle &= 2^{-1/2}(|\alpha\beta\alpha\rangle + |\beta\alpha\alpha\rangle) \\ |T_{-1}^{(1,2)}\alpha^{(3)}\rangle &= |\beta\beta\alpha\rangle \\ |T_{+1}^{(1,2)}\beta^{(3)}\rangle &= |\alpha\alpha\beta\rangle \\ |T_0^{(1,2)}\beta^{(3)}\rangle &= 2^{-1/2}(|\alpha\beta\beta\rangle + |\beta\alpha\beta\rangle) \\ |T_{-1}^{(1,2)}\beta^{(3)}\rangle &= |\beta\beta\beta\rangle \end{aligned} \tag{15}$$

These kets may be classified in terms of their total angular momentum quantum number M along the z-axis, for example

$$\begin{aligned} I_z|T_{+1}^{(1,2)}\alpha^{(3)}\rangle &= \tfrac{3}{2}|T_{+1}^{(1,2)}\alpha^{(3)}\rangle \\ I_z|T_{+1}^{(1,2)}\beta^{(3)}\rangle &= \tfrac{1}{2}|T_{+1}^{(1,2)}\beta^{(3)}\rangle \\ I_z|T_0^{(1,2)}\alpha^{(3)}\rangle &= \tfrac{1}{2}|T_0^{(1,2)}\alpha^{(3)}\rangle \end{aligned} \tag{16}$$

and so on. Since the coupling Hamiltonian commutes with I_z, and the singlet and triplet kets are all eigenkets of I_z, the matrix representation of the coupling Hamiltonian is block-diagonal in the basis spanned by the singlet states in Eq. (12) and the triplet states in Eq. (15). There are two one-dimensional blocks (one state each with $M = \pm 3/2$) and two three-dimensional blocks (three states each with $M = \pm 1/2$).

Consider the $M = +1/2$ block, which is spanned by the states $\{|S_0^{(1,2)}\alpha^{(3)}\rangle, |T_0^{(1,2)}\alpha^{(3)}\rangle, |T_{+1}^{(1,2)}\beta^{(3)}\rangle\}$. The corresponding block of the J-coupling Hamiltonian matrix is given by

$$\mathcal{H}_J = \begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \\ \cdots & -\frac{3}{2}\pi J_{12} & \frac{1}{2}\pi J_\Delta & -\frac{1}{\sqrt{2}}\pi J_\Delta & \cdots \\ \cdots & \frac{1}{2}\pi J_\Delta & \frac{1}{2}\pi J_{12} & \frac{1}{\sqrt{2}}\pi J_\Sigma & \cdots \\ \cdots & -\frac{1}{\sqrt{2}}\pi J_\Delta & \frac{1}{\sqrt{2}}\pi J_\Sigma & \frac{1}{2}\pi J_{12} - \frac{1}{2}\pi J_\Sigma & \cdots \\ & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \tag{17}$$

where the sum and difference of the out-of-pair couplings are:

$$\begin{aligned} J_\Sigma &= J_{13} + J_{23} \\ J_\Delta &= J_{13} - J_{23} \end{aligned} \tag{18}$$

Investigation of Eq. (17) shows under which conditions the out-of-pair J-couplings become ineffective. The diagonal element of $\mathcal{H}_J$ corresponding to the singlet state is separated from the diagonal elements corresponding to the two triplet states by $2\pi J_{12}$ and $2\pi J_{12} - \frac{1}{2}\pi J_\Sigma$, respectively, where J_{12} is the intra-pair J-coupling. The off-diagonal elements connecting the singlet state to the two triplet states are of the order of πJ_Δ. The secular approximation states that off-diagonal matrix elements may be ignored if they are smaller than the difference in the connected diagonal elements. The influence of the out-of-pair couplings on the singlet state is therefore suppressed if the following conditions are satisfied:

$$|J_{12}| \gg \tfrac{1}{4}|J_{13} - J_{23}|$$
$$|J_{12}| - \tfrac{1}{2}J_{13} - \tfrac{1}{2}J_{23} \gg \tfrac{1}{2\sqrt{2}}|J_{13} - J_{23}| \quad (19)$$

Both conditions are satisfied simultaneously if the intra-pair J-coupling J_{12} is much larger than both out-of-pair J-couplings.

The $M = -1/2$ block of the coupling Hamiltonian leads to similar conclusions.

4. Methods

The simulations in Figs. 1 and 2 were performed using Mathematica version 5.2 [18], assisted by the mPackages routines, which are available from the authors at http://www.mhl.soton.ac.uk/public/software/mPackages/.

5. Conclusions

The identification of a stabilization mechanism which protects singlet states against long-range J-couplings is gratifying. Without this mechanism, it would be hard to understand the experimental observations of long-lived singlet states in multiple-spin molecules.

The intra-pair J-coupling does not protect singlet states from the dipole–dipole relaxation induced by distant spins. In molecules containing many spins, multiple dipole–dipole couplings usually cause relatively fast relaxation of singlet states, compared to the isolated two-spin case. Nevertheless, the singlet lifetimes may be more than an order of magnitude longer than T_1, in realistic experimental situations.

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