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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.

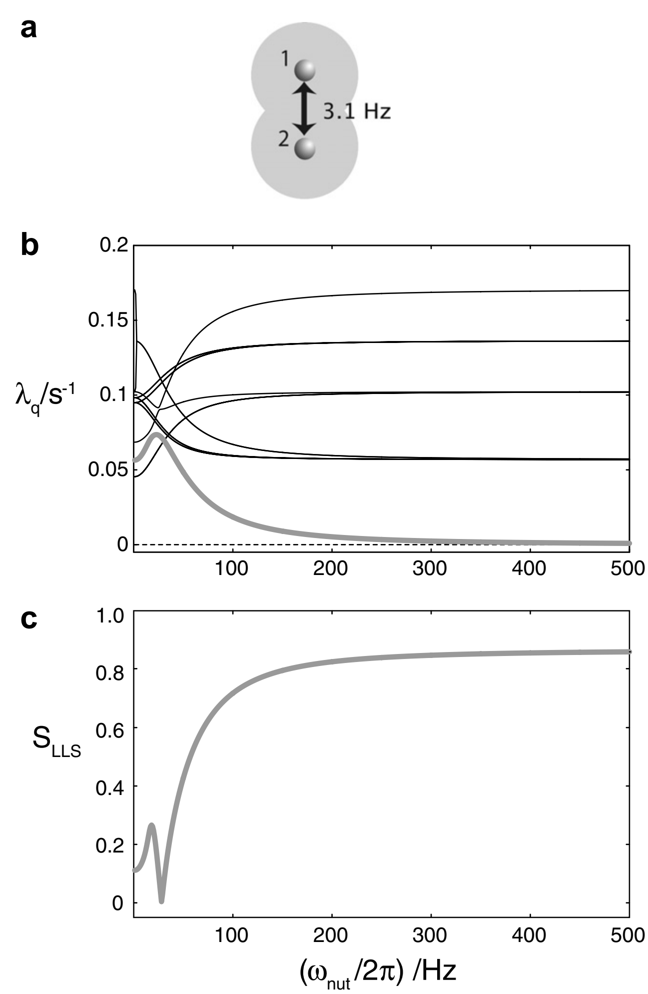

Fig. 1. (a) Two-spin system used in the simulation. The simulation parameters are: chemical shift frequency difference = 76.0 Hz; J-coupling = 3.1 Hz; dipole–dipole coupling = −18.5 kHz; rotational correlation time = 8.4 ps. (b) Decay rate constants of the Liouvillian eigenoperators, as a function of 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}.