Multiple decoherence-free states in multi-spin systems

H.J. Hogben a,⁎, P.J. Hore a, Ilya Kuprov b

a Department of Chemistry, University of Oxford, Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, UK
b Oxford e-Research Centre, University of Oxford, 7 Keble Road, Oxford OX1 3QG, UK

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A B S T R A C T
A numerical procedure is presented for mapping the vicinity of the null-space of the spin relaxation superoperator. The states populating this space, i.e. those with near-zero eigenvalues, of which the two-spin singlet is a well-studied example, are long-lived compared to the conventional T1 and T2 spin-relaxation times. The analysis of larger spin systems described herein reveals the presence of a significant number of other slowly relaxing states. A study of coupling topologies for n-spin systems (4 ≤ n ≤ 8) suggests the symmetry requirements for maximising the number of long-lived states.

1. Introduction
An ability to tame spin relaxation by finding the rare states that resist the gradual drift towards thermal equilibrium [1–3] is of considerable interest in magnetic resonance. The slowly relaxing states may be used to store polarisation [4–7], measure slow diffusion [8], and obtain information on molecular structure [9]. Such super-stable states were recently found to exist in dipolar-coupled spin systems [1] and have since attracted much theoretical [7,10–12] and experimental [2,7,8,11] attention. Their common property – a zero dipolar relaxation rate – can be formulated as defining the null space of the relaxation superoperator to which their associated eigenvectors belong. More generally, we are interested in finding those eigenstates of the full relaxation superoperator that have small (but not necessarily zero) eigenvalues. Analytical treatments are possible for small systems [3,10–12], but collections of more than four spins have not hitherto been studied systematically.

Drawing on our recent work on large-scale spin dynamics simulations [13–15] and construction of relaxation superoperators [16] for large spin systems, we report here a systematic mapping of the dipolar relaxation null spaces for systems with four to eight spins using the Spinach software library [17]. Investigation of different spin-½ coupling topologies evinces clear symmetry and coupling requirements for maximising the number of long-lived states.

The null-space analysis follows a simple procedure: build the Liouvillian and find the eigenvectors corresponding to zero or near-zero eigenvalues [12,18]. Different dipolar coupling topologies comprising at least four spins are predicted to have more than one non-trivial (i.e. other than the identity operator) long-lived state when certain symmetry requirements are met. These criteria are illustrated with three examples of commercially available molecules expected to exhibit multiple long-lived states in liquid state NMR experiments.

2. Theoretical formalism
In order to be long-lived, a state $\hat{\rho}$ or a subspace of states $K = \text{span}\{\hat{\rho}_1, \ldots, \hat{\rho}_k\}$ must be invariant with respect to time evolution under the system Liouvillian $\hat{L}$:

$$\exp\left(-i\hat{L}t\right)\hat{\rho} = \hat{\rho} \Rightarrow \left(\sum_{n=0}^{\infty} \frac{\left(-it\right)^n}{n!} \hat{L}^n\right)\hat{\rho} = \hat{\rho} \Rightarrow$$

$$\hat{\rho} + \sum_{n=1}^{\infty} \frac{\left(-it\right)^n}{n!} \hat{L}^n\hat{\rho} = \hat{\rho} \Rightarrow \sum_{n=1}^{\infty} \frac{\left(-it\right)^n}{n!} \hat{L}^n\hat{\rho} = 0 \quad \forall t \in [0, \infty),$$

where $\hat{L} = \hat{H} + i\hat{K}, \hat{H}$ is the Hamiltonian commutation superoperator and $\hat{K}$ is the relaxation superoperator. This invariance is only possible (as a consequence of the Taylor expansion uniqueness theorem) if $\hat{\rho}$ or $K$ belongs to the null space of the Liouvillian:

$$\hat{L}\hat{\rho} = 0 \quad \hat{L} : \hat{K} \rightarrow \{0\}$$

The general task of finding long-lived states in a particular system therefore amounts to finding the null space of the system Liouvillian. Control of the coherent part of the Liouvillian (contained in $\hat{H}$) is well developed: field-shuttling, spin-locking and

⁎ Corresponding author.
E-mail address: hannah.hogben@chem.ox.ac.uk (H.J. Hogben).

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decoupling can be used to halt the evolution of states of interest under the influence of chemical shift differences or external J-couplings [11,12,19]. There remains the part of the Liouvillian that we cannot normally control – the incoherent relaxation processes – which has yet to be fully exploited from a practical perspective. Accordingly, we shall focus our attention on the relaxation superoperator and look for states that are immune to it. The most general formulation of spin-relaxation theory for spin systems with a one-way coupling to a classical heat bath is [20,21]:

\[
\tilde{\sigma}(t + \Delta t) = \tilde{\sigma}(t) + \sum_{n=1}^{\infty} (-i)^n \int_0^{\infty} dt_1 \int_0^{t_1} dt_2 \ldots \int_0^{t_{n-1}} dt_n \hat{H}_I(t_1)\hat{H}_I(t_2)\ldots\hat{H}_I(t_n) \tilde{\sigma}(t)
\]

where \(\langle \cdot \rangle\) denotes ensemble average, \(\tilde{\sigma}(t)\) is the ensemble average density matrix and \(\hat{H}_I(t)\) is the stochastic part of the Liouvillian commutation superoperator, both written in the interaction representation with respect to the coherent Liouvillian. Truncation of this series at the second order with some additional assumptions is known in magnetic resonance as Bloch–Redfield–Wangsness relaxation theory [22,23]. As most semi-classical theories do, this formalism relaxes the system to the infinite temperature state. This is expected. An example of MATLAB code calling the Spinach library [17], the resulting relaxation superoperator was diagonalised and the eigenvectors corresponding to small eigenvalues were inspected. An example of MATLAB code calling the Spinach library for this purpose can be found in Supplementary information along with the console output that lists all the interaction parameters.

\[
\tilde{\sigma}(t + \Delta t) = \tilde{\sigma}(t) + \sum_{n=1}^{\infty} (-i)^n \int_0^{\infty} dt_1 \int_0^{t_1} dt_2 \ldots \int_0^{t_{n-1}} dt_n \hat{H}_I(t_1)\hat{H}_I(t_2)\ldots\hat{H}_I(t_n) \tilde{\sigma}(t)
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It is clear from Eq. (3) that a sufficient condition for a state to be immune to propagation under the relaxation superoperator is belonging to the null space of the stochastic Hamiltonian commutation superoperator at all times:

\[
\hat{H}_I(t)\tilde{\sigma} = 0 \Rightarrow e^{i\hat{H}_I(t)}\hat{H}_I(t)e^{-i\hat{H}_I(t)}\tilde{\sigma} = 0 \Rightarrow \hat{H}_I(t)\tilde{\sigma} = 0.
\]

Whether or not this is also a necessary condition, we do not know – this seems unlikely, because terms could in principle cancel or vanish under the average in Eq. (3). This explains why singlet states are immune to dipolar relaxation (the singlet density matrix commutes with the dipolar Hamiltonian involving the two spins in question and with any operator that does not affect those spins) and provides a rapid test for the long-lived character of a state of interest. In particular any state from which all transitions under \(\hat{H}_I(t)\) are permutation-symmetry-forbidden is going to be long-lived. However, all of the long-lived states (including those where the eigenvalue is very small but non-zero) can only be discovered with certainty by mapping the null-space of the full relaxation superoperator in square brackets in Eq. (3).

Before embarking on larger systems, we shall briefly review the classic two-spin case [1]. For a dipolar-coupled pair of spins-½ the null space of the relaxation superoperator is spanned by two states. If only dipolar relaxation is considered, the eigenvalues are exactly zero and the states persist indefinitely. Any linearly independent pair of states (they do not have to be orthogonal) may be chosen as the basis of this two-dimensional null space, for example:

\[
\tilde{1} = \tilde{P}_x + \tilde{P}_y + \tilde{P}_z + \tilde{P}_S \quad \text{and} \quad \tilde{P}_S = \tilde{P}_x + \tilde{P}_y + \tilde{P}_z - \tilde{P}_S
\]

where \(\{\tilde{P}_x, \tilde{P}_y, \tilde{P}_z, \tilde{P}_S\}\) are projectors into the singlet and the three triplet states. The identity operator 1 is not interesting because it commutes with any Hamiltonian and will hereafter be omitted from the discussion. The \(\tilde{P}_S\) state is the difference between the singlet state, \(\tilde{P}_S\), and the sum of the three triplet states. Any linear combination of these states is also in the null space and is thus also long-lived. A particularly convenient (on symmetry grounds) linear combination, known as the “the” singlet state may be written in the usual \[\beta\] basis set as:

\[
\tilde{P}_S = \frac{1}{2}[(\beta|\beta\rangle - |\beta\beta\rangle)](\langle \beta|\beta\rangle - \langle \beta\beta\rangle).
\]

3. Results and discussion

A systematic search to find long-lived states by mapping the null space of the full relaxation superoperator has been performed on dipolar coupled systems with three to eight spin-½ nuclei. A range of system symmetries and coupling patterns was investigated; the results are summarised in Fig. 1 in which coupling topologies are grouped according to the number of long-lived states found in them. A nearest neighbour separation of 1 Å was chosen (to give a dipolar coupling of \(D \approx 120\) kHz); being just
shorter than a $^{13}$C–$^1$H bond length this provides an upper bound on the dipolar interactions likely to be encountered in organic molecules. All pair-wise dipolar interactions were included in the relaxation superoperator with coupling constants and dipolar axes calculated from the geometry of the spin system.

For a dipolar coupled three-spin-system only the linear geometry returns a long-lived state as was shown analytically in Ref. [26]. For larger systems it appears that only the topologies that have a centre of inversion show any long-lived states at all. This is to be expected for the dipolar relaxation superoperator, which inherits the symmetry of Eq. (7) with respect to the permutation of the two spins. The long-lived states are not formed from combinations of singlets across the most strongly coupled pairs, i.e. those with minimum separation, but instead from the symmetric combinations of products of singlets across the spins interchanged by the inversion symmetry. For example, the square $D_{4h}$ four-spin system yields a non-trivial null-space state:

$$4P_S^{(1,3)}P_S^{(2,4)} - 1$$

The number of linear combinations of eigenvectors with small eigenvalues do themselves have small eigenvalues, it is possible to take an alternative linear combination of the state in Eq. (8) with its identity operator partner to yield the more intuitively recognisable $P_S^{(1,3)}P_S^{(2,4)}$. This demonstrates the localised singlet character of the inversion-related spins, i.e. of those across the diagonal of the square which experience the weaker of the two dipolar coupling amplitudes in the system. The same state, with its triplet mixture counterpart, also forms a part of the null space of the linear four-spin system (Fig. 1), along with two further mixed states. An isolated singlet state across any pair of spins in that system does not appear anywhere in the null space and thus would not exhibit slow relaxation. This may be confirmed by substituting of the requisite states into Eq. (4) which fails to return the all-zero vector indicative of long-lived character.

Multi-spin systems are known to have a long-lived state when a localised singlet interacts only weakly with neighbouring spins [3]. Coupling topologies combining strong ($D \approx 120$ kHz) and weak ($D \approx 120$ Hz) interactions were therefore investigated with the results shown in Fig. 2 and Supplementary information Table S1. Four-spin systems, of $C_1$ and $D_{2h}$ symmetry, have been observed experimentally to display a long-lived state [27]. The nature of the observed state was proposed to be a singlet localised on one of the two pairs of strongly coupled spins stabilised by the $J$-coupling within the pair [18]. The results from our analysis, shown in

Fig. 2, demonstrate that this is certainly possible but that a more complicated product of singlets may also be responsible for the long lifetime observed. The states in addition to the isolated singlets are either products of the strongly dipolar-coupled singlets or symmetric linear combinations across all pair-wise singlet permutations. The number of long-lived states available is maximised when sets of strongly coupled pairs are related by centres of inversion, more precisely by an inversion with respect to the midpoint of the pairs, not necessarily the centre of inversion of the whole system. The state vectors are linear combinations or products of localised singlets across all pairs of symmetry related spins, even if they have only a weak dipolar coupling. As the interactions between sets of strongly coupled pairs increases the long-lived states are increasingly perturbed and the non-symmetric linear combinations mix so as to increase the eigenvalues of the relaxation matrix, reducing the long-lived states to those shown in Fig. 1.

Having established the symmetry and coupling pattern requirements for the presence of multiple long-lived states, we have investigated three apparently suitable molecules, Fig. 3. They were chosen primarily for the symmetry of their dipolar coupling networks but also for their relatively small CSA. The eigenvalues of

Table 1

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<tr>
<th>Molecule</th>
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Fig. 3. Molecules expected to show long lived states.
the system Liouvillian were calculated for three cases: dipolar relaxation superoperator only, full relaxation superoperator (including CSA) only, and finally the total Liouvillian that includes also the coherent evolution for the molecule in a moderate (1 Tesla) static field. Table 1 shows the 10 smallest amplitude eigenvalues in each instance; long-lived states are defined as those that have eigenvalues more than an order of magnitude smaller than the majority.

Each molecule reveals six non-trivial long-lived states, that is, six states that would resist relaxation if coherent evolution is suppressed. In the presence of unsuppressed coherent evolution, bicyclopropylidene-d₄ (1) naphthalenetetrone (2) and p-benzoquinone (3) all have only one extremely long-lived state, which has an eigenvalue seven orders of magnitude smaller than the average. Reducing the field strength, or using other methods to limit coherent evolution, moves the eigenvalues towards the relaxation-only limit, that is, the six usable states identified in Fig 2. Molecules with more sets of inversion-related dipolar coupled pairs should exhibit even more long-lived states.

4. Conclusion

We have presented a method with which to determine the number and identity of the states in multi-spin systems that are immune or insensitive to dipolar relaxation. Using this procedure we have identified some general requirements to maximise the number of long-lived states. Firstly, for a strongly coupled spin system to exhibit long-lived states, some spin pairs must be related by an inversion symmetry. Multiple pairs of strongly dipolar-coupled spins with only weak inter-pair interactions lead to many long-lived states when there are 'pairs of pairs' related to each other by a centre of inversion. We have identified large slowly relaxing subspaces in several commercially available molecules. Their existence provides scope for using these and other such molecules as hyperpolarising agents in magnetic resonance experiments.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jmr.2011.06.001.

References