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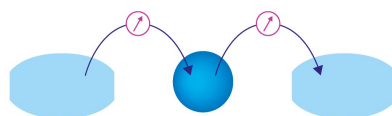
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ABSTRACT

We provide a theoretical analysis of spin-selective recombination processes in clusters of $n \geq 3$ radicals. Specifically, we discuss how spin correlation can ensue from random encounters of n radicals, i.e., “F-clusters” as a generalization of radical F-pairs, acting as precursors of spin-driven magnetic field effects. Survival probabilities and the spin correlation of the surviving radical population, as well as transients, are evaluated by expanding the spin density operator in an operator basis that is closed under application of the Haberkorn recombination operator and singlet–triplet dephasing. For the primary spin cluster, the steady-state density operator is found to be independent of the details of the recombination network, provided that it is irreducible; pairs of surviving radicals are triplet-polarized independent of whether they are actually reacting with each other. The steady state is independent of the singlet–triplet dephasing, but the kinetics and the population of sister clusters of smaller size can depend on the degree of dephasing. We also analyze reaction-induced singlet–triplet interconversion in radical pairs due to radical scavenging by initially uncorrelated radicals (“chemical Zeno effect”). We generalize previous treatments for radical triads by discussing the effect of spin-selective recombination in the original pair and extending the analysis to four radicals, i.e., radical pairs interacting with two radical scavengers.

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I. INTRODUCTION

Spin dynamics can render chemical reactions magnetosensitive.^{1–3} The Radical Pair Mechanism (RPM) is such an example.^{4–6} Here, magnetosensitivity emerges as the result of the magnetic field-dependent interconversion of electronic singlet and triplet states of a pair of radicals in combination with spin state-discriminating reaction pathways. These magnetic field effects are not a result of equilibrium states affected by the presence of the magnetic field but are attributed to the decoherence of non-equilibrium electronic spin states, such as the singlet or triplet states, while coupling to their surroundings, e.g., nuclear spins via hyperfine interactions. The magnetic field alters the spin dynamics of these processes by biasing the energy levels of the combined electron and nuclear spin system. As the spins are only weakly coupled to the space degrees of freedom and, thus, noise processes, the spin correlations can be long-lived, which allows sensitivity to weak magnetic fields even if the Zeeman interaction energy of the field with an electron spin is entirely negligible compared to $k_B T$.⁷ This puts the radical pair

mechanism in the spotlight of quantum biology,⁸ where it is predominantly discussed in the context of the avian, cryptochrome-based, visual compass.⁹ However, the mechanism has been broadly researched since the 1960s, with many examples of magnetosensitive radical reactions provided in the literature.¹ The reader is directed to one of several excellent review articles on this topic for details.^{1,2,5,6}

The central element of the RPM is the spin-correlated radical pair.^{1,2,5,6} These non-equilibrium spin states most often result from the chemical reactions that generate the radical pair, e.g., electron and hydrogen transfer processes or homolytic bond cleavage. In the absence of marked spin–orbit coupling, these reactions conserve the total electron spin. Thus, diamagnetic precursors give rise to radical pairs in the singlet state, while triplet precursors, such as photo-excited molecular triplet states of chromophores, lead to triplet radical pairs. Emanating from a common reaction process, such radical pairs are referred to as *geminat*e radical pairs.

Geminate processes are not the only source of spin correlation. Radical encounters of uncorrelated radicals can give

rise to non-equilibrium spin configurations when spin-selective recombination pathways exist. These F-pair radicals (“F” for freely diffusing) initially encounter one another with a random relative spin orientation, which corresponds to the thermalized state of such systems, expressible as a mixture of 3/4 triplet and 1/4 singlet electron spin pairs.^{2,10,11} If such pairs predominantly recombine in one angular momentum state, spin correlation can still ensue by depopulating one spin configuration relative to the other. Thus, assuming an efficient singlet recombination process, in the first encounter of uncorrelated radicals, 1/4 of the pairs will recombine, while the 3/4 corresponding to triplet encounters will survive, poised to undergo potentially magnetosensitive spin dynamics affecting subsequent encounters. Although spin dynamics and recombination will often happen simultaneously, this schematic picture still provides a qualitative understanding of the ensuing magnetic field sensitivity.

The potential magnetosensitivity of the recombination dynamics is not an exclusive feature of radical pairs. Systems of n radicals ($n \geq 3$) have been suggested to acquire magnetosensitivity as a result of their mutual electron–electron dipolar coupling, even in the absence of the otherwise crucial hyperfine interactions or differences in electron g -factors.^{12,13} This mechanism, here referred to as DnM , has been suggested to underpin magnetic field effects in lipid peroxidation¹⁴ and to perturb or boost the avian compass.¹⁵ Clusters, instead of pairs, of radicals are also conceivable in processes implicated with high local radical concentrations, such as ferroptosis¹⁶ or spurs of ionizing radiation.^{17,18} Radiation spurs typically contain more than two free radicals in a narrow spatially correlated distribution, usually generated with an overall singlet configuration.¹⁷ Spin effects on the fast, diffusion-controlled recombination kinetics of such radical clusters have been studied at various levels of approximation.^{17,19–22} Most notably, the coherent buildup of electron polarization has been studied by a simultaneous random flight simulation of diffusive trajectories and integration of the time-dependent Schrödinger equation (including Zeeman and exchange interactions) for four radicals.²² Comparable effects could, in principle, contribute to the multi-polaron recombination in organic semiconductors.^{6,23}

The reaction-induced dynamics of spin systems are surprisingly rich in features. If a radical pair reacts with a third, initially uncorrelated radical, the reaction induces singlet–triplet conversion in the original pair, even in the absence of coherent interconversion pathways.²⁴ This effect, which was suggested by Letuta and Berdinskii and was dubbed the “chemical Zeno effect” (although the chemical anti-Zeno effect might better reflect its properties), can give rise to large magnetic field effects when combined with the usual hyperfine-driven spin dynamics, as we have shown in the context of the avian compass model,^{25,26} and can be used to teleport spin states.²⁷ For more than three spin-selectively recombining radicals, even richer effects are expected. Green *et al.* pointed out that for a configuration of four radicals in an overall singlet state composed of singlet pairs, pairs are subject to unexpected non-local correlations.¹⁹ If, for example, pairs (1, 2) and (3, 4) in such a radical cluster are singlet, then all the other possible pairings [including (1, 3), (1, 4), (2, 3), and (2, 4)] are random (with a singlet probability of 1/4). Then, if pair (1, 3) was randomly encountered and was found in the singlet, i.e., reactive, state, the collapse of the wavefunction would cause the disjoint pair (2, 4) to also become singlet.

This contribution addresses a simple question: Given a system of n radicals subject to an arbitrary reaction network of mutually spin-selective recombination processes, what is the non-equilibrium spin configuration of the radical population surviving the encounter? We are interested in fast-recombination effects that generate spin correlation merely by spin-selective recombination, without significant coherent dynamics. The resulting correlated spin configurations could however be the starting point of subsequent slower spin dynamics, potentially leading to versatile magnetic field effects.

II. MODEL

Our model aims to describe the reaction-induced spin correlation created in encounters of reactive radicals. We consider clusters of n radicals subject to pairwise recombination in the singlet state and neglect coherent evolution and spin relaxation. The dynamics of these systems can be described in the direct product Hilbert space of the n electron spins. The electronic spin density operator $\hat{\rho}(t)$ obeys an equation of motion of the form

$$\frac{d\hat{\rho}(t)}{dt} = -\sum_{i < j} \hat{K}_{i,j} \hat{\rho}(t) = -\sum_{i < j} (\hat{K}_{i,j} + \hat{K}'_{i,j}) \hat{\rho}(t), \quad (1)$$

where $\hat{K}_{i,j}$ accounts for the recombination of the radical pair labeled i and j . $\hat{K}_{i,j}$ can be written as the sum of the Haberkorn reaction operator, $\hat{K}'_{i,j}$, and a term that accounts for additional, reaction-induced singlet–triplet dephasing of the (i, j) -pair, $\hat{K}''_{i,j}$.²⁸ For a singlet recombination reaction, the former is given by²⁹

$$\hat{K}'_{i,j} \hat{\rho}(t) = \frac{k_{i,j}}{2} \{ \hat{P}_S^{(i,j)}, \hat{\rho}(t) \}, \quad (2)$$

where $\{ \}$ denotes the anticommutator and $\hat{P}_S^{(i,j)}$ denotes the singlet projection operator, i.e.,

$$\hat{P}_S^{(i,j)} = \sum_{\{y\}} |S_{ij}, \{y\}\rangle \langle S_{ij}, \{y\}| = \frac{1}{4} \hat{1} - \frac{1}{\hbar^2} \hat{S}_i \cdot \hat{S}_j, \quad (3)$$

with $\{y\}$ denoting quantum numbers other than those specifying spins i and j and $|S_{ij}\rangle = \frac{1}{\sqrt{2}} (|\uparrow\rangle_i |\downarrow\rangle_j - |\downarrow\rangle_i |\uparrow\rangle_j)$, where $|\uparrow\rangle_i$ and $|\downarrow\rangle_i$ are the eigenstates of \hat{S}_i^z and $\hat{S}_{i,z}$ with projections $\hbar/2$ and $-\hbar/2$, respectively. As triplet recombination could always be reformulated as a homogeneous decay and singlet growth, it does not add additional intricacies; this case will not be considered.

$\hat{K}''_{i,j}$ can be written as³⁰

$$\begin{aligned} \hat{K}''_{i,j} \hat{\rho}(t) &= k'_{i,j} \left(\hat{P}_S^{(i,j)} \hat{\rho}(t) \hat{P}_T^{(i,j)} + \hat{P}_T^{(i,j)} \hat{\rho}(t) \hat{P}_S^{(i,j)} \right) \\ &= k'_{i,j} \left(\{ \hat{P}_S^{(i,j)}, \hat{\rho}(t) \} - 2 \hat{P}_S^{(i,j)} \hat{\rho}(t) \hat{P}_S^{(i,j)} \right), \end{aligned} \quad (4)$$

with $\hat{P}_T^{(i,j)} = \hat{1} - \hat{P}_S^{(i,j)}$ denoting the triplet projection operator associated with spin pair (i, j) . The singlet–triplet decoherence rate

constant k'_{ij} is expected to depend on the characteristics of the recombination processes.²⁸ For the particular choice $k'_{ij} = k_{ij}/2$, Eq. (1) reduces to the Jones–Hore model.^{31,32} Haberkorn’s original phenomenological model assumed $k'_{ij} = 0$, i.e., minimal singlet–triplet dephasing (ST-dephasing).²⁹ While this minimal model has some theoretical backing,^{33–35} it has also been criticized for underestimating the degree of singlet–triplet decoherence.³⁶ Nonetheless, likely because sources of singlet–triplet decoherence are ample and not readily distinguishable in most practical cases,³⁷ the Haberkorn model is most frequently employed. The reaction-induced ST-dephasing is also a central theme of an alternative approach by Kominis.^{38,39}

Here, we solve Eq. (1) for F-pair-like encounters of n radicals, “F-cluster,” i.e., random initial spin distributions given by

$$\hat{\rho}(t=0) \equiv \hat{\rho}_0^{(F)} = \frac{1}{2^n} \hat{1}. \quad (5)$$

In addition, we will provide results for the case that one spin pair is born in a singlet or triplet configuration within a bath of $(n-2)$ uncorrelated spins, i.e., $\hat{\rho}(0) \propto \hat{P}_S^{(ij)}$ or $\hat{\rho}(0) \propto \hat{P}_T^{(ij)}$. We will evaluate the survival probability of the n -spin system,

$$p = \lim_{t \rightarrow \infty} \text{Tr}[\hat{\rho}(t)], \quad (6)$$

and the survived singlet probability of pairs of spins,

$$p_S^{(ij)} = \lim_{t \rightarrow \infty} \text{Tr}[\hat{P}_S^{(ij)} \hat{\rho}(t)]. \quad (7)$$

The singlet probability conditioned on survival is $p_S^{(ij)}/p$.

III. A SIMPLE EXAMPLE

We provide a simple, illustrative example; the general approach will be outlined in Sec. IV. Let us consider a system of three radicals in a linear configuration for which nearest neighbors recombine in the singlet state at the same rate, i.e., $n = 3$, $k_{1,2} = k_{2,3} = k$, and $k_{1,3} = 0$. Let us also neglect ST-dephasing, i.e., $k'_{ij} = 0$. Thus, the pertinent equation of motion is

$$\begin{aligned} \frac{d\hat{\rho}(t)}{dt} &= -\frac{k}{2} \{ \hat{P}_S^{(1,2)}, \hat{\rho}(t) \} - \frac{k}{2} \{ \hat{P}_S^{(2,3)}, \hat{\rho}(t) \} \\ &= -\frac{k}{2} \{ \hat{P}_S^{(1,2)} + \hat{P}_S^{(2,3)}, \hat{\rho}(t) \} \\ &\equiv -\frac{k}{2} \{ \hat{R}, \hat{\rho}(t) \}, \end{aligned} \quad (8)$$

where we have introduced $\hat{R} \equiv \hat{P}_S^{(1,2)} + \hat{P}_S^{(2,3)}$. The solution of this system can formally be expressed as a Maclaurin series,

$$\hat{\rho}(t) = \sum_{m=0}^{\infty} \frac{t^m}{m!} \hat{\rho}^{(m)}(t=0). \quad (9)$$

This series is guaranteed to converge for all t because the solution of Eq. (1) or (8) is entire, i.e., expressible as the exponent of the Liouvillian, which is entire. For $\hat{\rho}(t=0) \equiv \hat{\rho}_0^{(F)}$, the m -th derivative at time $t=0$ is given by

$$\hat{\rho}^{(m)}(t=0) = \frac{(-1)^m k^m}{2^{m+n-1}} \underbrace{\{ \hat{R}, \{ \hat{R}, \dots \{ \hat{R}, \hat{\rho} \} \} \}}_{(m-1) \text{ anticommutators}}. \quad (10)$$

The nested anticommutator comprises a total of m \hat{R} terms (obviously, the nested anticommutators could be rewritten as the m -th power of \hat{R} ; we retain the anticommutator form as it more closely resembles the general approach outlined below). The form of Eq. (10) suggests that Eq. (8) could be solved by finding a set of operators $\{ \hat{B}_\ell \}$ that contains $\hat{\rho}(0)$ and is closed under repeated application of the anticommutator, i.e.,

$$\left\{ \hat{B}_\ell \left| \{ \hat{R}, \hat{B}_\ell \} = \sum_j b_j \hat{B}_j, b_j \in \mathbb{C} \right. \right\} \supseteq \{ \hat{\rho}(0) \}. \quad (11)$$

We can then solve Eq. (8) using the ansatz

$$\hat{\rho}(t) = \sum_\ell c_\ell(t) \hat{B}_\ell. \quad (12)$$

An explicit calculation shows that

$$\hat{\rho}^{(2)}(t) \propto \frac{1}{2} \{ \hat{R}, \hat{R} \} = \hat{R} + \{ \hat{P}_S^{(1,2)}, \hat{P}_S^{(2,3)} \}. \quad (13)$$

Further application of the anticommutator, thus, gives rise to a term of the already encountered form $\{ \hat{R}, \hat{R} \}$ and the one proportional to

$$\begin{aligned} \frac{1}{2} \{ \hat{R}, \{ \hat{P}_S^{(1,2)}, \hat{P}_S^{(2,3)} \} \} &= \{ \hat{P}_S^{(1,2)}, \hat{P}_S^{(2,3)} \} + \hat{P}_S^{(1,2)} \hat{P}_S^{(2,3)} \hat{P}_S^{(1,2)} \\ &\quad + \hat{P}_S^{(2,3)} \hat{P}_S^{(1,2)} \hat{P}_S^{(2,3)}. \end{aligned} \quad (14)$$

This result is actually closed in the set of operators already encountered. A detailed analysis of the recoupling behavior of three spins, which is provided in the Appendix and utilized in the general approach, reveals that the last two terms are, in fact, given by

$$\hat{P}_S^{(1,2)} \hat{P}_S^{(2,3)} \hat{P}_S^{(1,2)} + \hat{P}_S^{(2,3)} \hat{P}_S^{(1,2)} \hat{P}_S^{(2,3)} = \frac{1}{4} \hat{R}. \quad (15)$$

Taken together, Eqs. (13)–(15) show that in solution (11), only terms proportional to $\hat{1}$, $\hat{R} \equiv \hat{P}_S^{(1,2)} + \hat{P}_S^{(2,3)}$, and $\{ \hat{P}_S^{(1,2)}, \hat{P}_S^{(2,3)} \}$ occur. Hence, we write

$$\hat{\rho}(t) = c_1(t) \hat{1} + c_2(t) \hat{R} + c_3(t) \{ \hat{P}_S^{(1,2)}, \hat{P}_S^{(2,3)} \}, \quad (16)$$

which upon inserting in Eq. (8) and requiring that the resulting equations are individually fulfilled for the multipliers of every

basis operator (which is a necessity resulting from their linear independence) yields the following system of equations for the coefficients:

$$\begin{aligned}\dot{c}_1 &= 0, \\ \dot{c}_2 &= -k\left(c_1 + c_2 + \frac{1}{4}c_3\right), \\ \dot{c}_3 &= -k(c_2 + c_3).\end{aligned}\quad (17)$$

Note that these equations result from the direct comparison of the coefficients associated with individual basis operators, i.e., regardless of their lacking orthonormality. Solving subject to the initial condition corresponding to $\hat{\rho}_0^{(F)}$, i.e., $c_1(0) = 1/8$ and $c_2(0) = c_3(0) = 0$, gives

$$\begin{aligned}\hat{\rho}(t) &= \frac{1}{8}\hat{1} + \left(\frac{1}{24}e^{-\frac{3}{2}kt} + \frac{1}{8}e^{-\frac{1}{2}kt} - \frac{1}{6}\right)\left(\hat{p}_S^{(1,2)} + \hat{p}_S^{(1,2)}\right) \\ &+ \left(\frac{1}{12}e^{-\frac{3}{2}kt} - \frac{1}{4}e^{-\frac{1}{2}kt} + \frac{1}{6}\right)\left\{\hat{p}_S^{(1,2)}, \hat{p}_S^{(2,3)}\right\},\end{aligned}\quad (18)$$

which for $t \rightarrow \infty$ corresponds to a survival probability of $p = 1/2$ and vanishing singlet probabilities $p_S^{(1,2)} = p_S^{(2,3)} = p_S^{(1,3)} = 0$. We will discuss further details in the context of the general solution below.

IV. GENERAL APPROACH AND RESULTS

A. The general approach

The general approach and results are derived from the following relations, which we present upfront:

$$\left\{\hat{p}_S^{(ij)}, \hat{1}\right\} = 2\hat{p}_S^{(ij)}, \quad (19a)$$

$$\left\{\hat{p}_S^{(ij)}, \hat{p}_S^{(ij)}\right\} = 2\hat{p}_S^{(ij)}, \quad (19b)$$

$$\left\{\hat{p}_S^{(ij)}, \hat{p}_S^{(jk)}\right\} = \frac{1}{2}\left(\hat{p}_S^{(ij)} + \hat{p}_S^{(jk)} - \hat{p}_S^{(ik)}\right), \quad (19c)$$

$$\left\{\hat{p}_S^{(ij)}, \hat{p}_S^{(ik)}\hat{p}_S^{(jl)}\right\} = \frac{1}{2}\left(\hat{p}_S^{(ik)}\hat{p}_S^{(jl)} + \hat{p}_S^{(ij)}\hat{p}_S^{(kl)} - \hat{p}_S^{(jk)}\hat{p}_S^{(il)}\right), \quad (19d)$$

$$\hat{p}_S^{(ij)}\hat{1}\hat{p}_S^{(ij)} = \hat{p}_S^{(ij)}, \quad (20a)$$

$$\hat{p}_S^{(ij)}\hat{p}_S^{(ij)}\hat{p}_S^{(ij)} = \hat{p}_S^{(ij)}, \quad (20b)$$

$$\hat{p}_S^{(ij)}\hat{p}_S^{(jk)}\hat{p}_S^{(ij)} = \frac{1}{4}\hat{p}_S^{(ij)}, \quad (20c)$$

$$\hat{p}_S^{(ij)}\hat{p}_S^{(ik)}\hat{p}_S^{(jl)}\hat{p}_S^{(ij)} = \frac{1}{4}\hat{p}_S^{(ij)}\hat{p}_S^{(kl)}. \quad (20d)$$

Here, we have assumed that $i \neq j \neq k \neq l$. The order of the spin indices in the superscripted brackets is immaterial. The non-trivial

identities result from the recoupling relations of three and four spins, as shown in the Appendix. The trivial relations have been included for completeness.

In order to solve Eq. (1), we again strive to derive an operator basis that is closed under application of all \hat{K}_{ij} . Starting from the identity operator $\hat{1}$, Eq. (19) reveals that for a general recombination network connecting n spins obeying Eq. (2), a suitable (but not orthonormal) basis is composed from all singlet projection operators and their (commuting) products such that every spin index appears at most once. In particular, the basis comprises the $n(n-1)/2$ singlet projectors $\hat{p}_S^{(ij)}$ and products of up to $\lfloor n/2 \rfloor$ mutually orthogonal singlet projection operators,

$$\bigcup_{m=0}^{\lfloor n/2 \rfloor} \bigcup_{(i_1j_1) \neq \dots \neq (i_mj_m)} \hat{p}_S^{(i_1j_1)}\hat{p}_S^{(i_2j_2)} \dots \hat{p}_S^{(i_mj_m)} \equiv \bigcup_{\ell=1}^d \hat{B}_\ell, \quad (21)$$

where the product over singlet projection operators involves no spin index more than once. For $m = 0$, this basis includes the identity operator; $m = 1$ corresponds to the set of all singlet projection operators, $\{\hat{p}_S^{(ij)} \forall 1 \leq i < j \leq n\}$. Introducing $\hat{p}_S^{(ij)} \equiv (i, j)$ for succinctness, for $n = 3$, the operator basis is thus provided by $\{\hat{1}, (1, 2), (1, 3), (2, 3)\}$ and for $n = 4$, it is provided by $\{\hat{1}, (1, 2), (1, 3), (1, 4), (2, 3), (2, 4), (3, 4), (1, 2)(3, 4), (1, 3)(2, 4), (1, 4)(2, 3)\}$. Because of Eq. (19), the basis given by Eq. (21) is closed under application of \hat{K}_{ij} . Specifically, the reaction involving a particular spin pair acting on the basis with zero, one, or two indices in common will generate a linear combination of basis operators again involving products of $\hat{p}_S^{(ij)}$ with no spin index appearing twice. Furthermore, based on the representation of the dephasing term \hat{K}_{ij}^t in terms of the Lindbladian, Eq. (4), and Eq. (20), one finds that it is also closed under \hat{K}_{ij}^t .

The basis given by Eq. (21) comprises a total of

$$\begin{aligned}d &= 1 + \binom{n}{2} + \frac{1}{2!}\binom{n}{4}\binom{4}{2} + \frac{1}{3!}\binom{n}{6}\binom{6}{2}\binom{4}{2} + \dots \\ &= \sum_{m=0}^{\lfloor n/2 \rfloor} \binom{n}{2m} \frac{(2m)!}{2^m m!} = \sum_{m=0}^{\lfloor n/2 \rfloor} \frac{n!}{2^m m! (n-2m)!}\end{aligned}\quad (22)$$

operators, including the identity, to model the recombination dynamics of n radicals. Here, each term corresponds to the number of ways to choose $2m$ spin indices from the integers up to n multiplied with the number of ways to arrange these indices in mutually exclusive pairs (as expressed in terms of the number of ways of picking two at a time and divided by the number of permutations of pairs, i.e., $m!$). d is also equal to the number of partitions of a set of n elements into singletons or pairs, the number of involution permutations on n letters, or the number of standard Young tableaux with n cells. The number of required operators or operator combinations steeply rises with n ; yet, for moderate n , the dimension of the basis amounts to only $\approx 1\%$ of the complete basis of the dimension 2^{2n} (the relative size is larger for small n , minimal for $n = 12$, and rises again for larger n ; see Fig. S1).

The following ansatz, with the basis operators taken from Eq. (21), can thus be used to solve Eq. (1):

$$\hat{\rho}(t) = \sum_{\ell=1}^d c_{\ell}(t) \hat{B}_{\ell}. \quad (23)$$

In particular, inserting Eq. (23) in Eq. (1) and requiring that the coefficient relations associated with each basis operator are independently fulfilled, we obtain a system of first-order ordinary differential equations of dimension d , which can be written as

$$\frac{d}{dt} \mathbf{c}(t) = -\mathbf{A} \mathbf{c}(t). \quad (24)$$

Here, $\mathbf{c}(t)$ collects all expansion coefficients $c_{\ell}(t)$ and the matrix \mathbf{A} depends on the recombination and ST-dephasing rate constants.

The form of Eq. (1) further suggests that, independent of n , the coefficient associated with the identity $\hat{1}$, henceforth denoted by $c_1(t)$, is constant, i.e.,

$$\frac{d}{dt} c_1(t) = 0. \quad (25)$$

The relations for the other coefficients depend on n and the reaction topology of the system.

B. Results for $n = 3$

Exemplarily, we provide the result for $n = 3$ assuming that all pairwise singlet recombination reactions of spins i and j are realized with rate constants k_{ij} and k'_{ij} (see the [supplementary material](#) for $n = 4$). With the help of Eqs. (19) and (20), we find that in the basis of $\{\hat{1}, \hat{P}_S^{(1,2)}, \hat{P}_S^{(1,3)}, \hat{P}_S^{(2,3)}\}$,

$$\mathbf{A} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ k_{1,2} & \frac{1}{4}(4k_{1,2} + k_{1,3} + k_{2,3}) & \frac{1}{4}(k_{1,2} - k_{2,3}) & \frac{1}{4}(k_{1,2} - k_{1,3}) \\ k_{1,3} & \frac{1}{4}(k_{1,3} - k_{2,3}) & \frac{1}{4}(k_{1,2} + 4k_{1,3} + k_{2,3}) & \frac{1}{4}(k_{1,3} - k_{1,2}) \\ k_{2,3} & \frac{1}{4}(k_{2,3} - k_{1,3}) & \frac{1}{4}(k_{2,3} - k_{1,2}) & \frac{1}{4}(k_{1,2} + k_{1,3} + 4k_{2,3}) \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -\frac{1}{2}(k'_{1,3} + k'_{2,3}) & -\frac{1}{2}k'_{2,3} & -\frac{1}{2}k'_{1,3} \\ 0 & -\frac{1}{2}k'_{2,3} & \frac{1}{2}(k'_{1,2} + k'_{2,3}) & -\frac{1}{2}k'_{1,2} \\ 0 & -\frac{1}{2}k'_{1,3} & -\frac{1}{2}k'_{1,2} & \frac{1}{2}(k'_{1,2} + k'_{1,3}) \end{pmatrix}. \quad (26)$$

The general solution of this system of differential equations is complicated and not particularly revealing. However, assuming that $k'_{ij} = 0$ and that all non-zero rate constants are equal, simple results can be obtained for the triangular configuration ($k_{1,2} = k_{1,3} = k_{2,3} = k$) and the linear chain ($k_{1,2} = k_{2,3} = k$ and $k_{1,3} = 0$). Assuming that the initial state is random, $\hat{\rho}(0) = \hat{\rho}_0^{(F)}$, we find

$$\hat{\rho}(t) = \frac{1}{8} \hat{1} + \frac{1}{12} \left(e^{-\frac{3}{2}kt} - 1 \right) \left(\hat{P}_S^{(1,2)} + \hat{P}_S^{(1,3)} + \hat{P}_S^{(2,3)} \right) \quad (27)$$

and

$$\hat{\rho}(t) = \frac{1}{8} \hat{1} + \frac{1}{12} \left(e^{-\frac{3}{2}kt} - 1 \right) \left(\hat{P}_S^{(1,2)} + \hat{P}_S^{(2,3)} \right) + \frac{1}{24} \left(3e^{-\frac{1}{2}kt} - e^{-\frac{3}{2}kt} - 2 \right) \hat{P}_S^{(1,3)} \quad (28)$$

for the linear chain and the triangular configuration, respectively. For both scenarios, the steady-state density operator, $\hat{\rho}_{\infty} = \lim_{t \rightarrow \infty} \hat{\rho}(t)$, is given by

$$\hat{\rho}_{\infty} = \frac{1}{8} \hat{1} - \frac{1}{12} \left(\hat{P}_S^{(1,2)} + \hat{P}_S^{(1,3)} + \hat{P}_S^{(2,3)} \right). \quad (29)$$

For this state, the singlet probability of any pair of spins vanishes, i.e., $p_S^{(ij)} = 0$.

C. Steady states

The steady state of any reaction system is contained in the null space (kernel) of \mathbf{A} , i.e.,

$$\frac{d\hat{\rho}_{\infty}}{dt} = 0 \Rightarrow \mathbf{A} \mathbf{c}_{\infty} = 0. \quad (30)$$

The null space, $\ker(\mathbf{A}) = \{\mathbf{x} \in \mathbb{R}^d | \mathbf{A}\mathbf{x} = 0\}$, will, in general, depend on the structure of the reaction network. Let us assume the most general reaction network with $k_{ij} \neq 0$ and $k'_{ij} \neq 0$ and attempt to find a vector in the kernel. For arbitrary k_{ij} and k'_{ij} , a sufficient condition for \mathbf{x} to be in $\ker(\mathbf{A})$ is that for the associated density operator, $\hat{\rho}_x = \sum x_{\ell} \hat{B}_{\ell}$, individually

$$\hat{K}_{ij} \hat{\rho}_x = 0 \quad \text{and} \quad \hat{K}'_{ij} \hat{\rho}_x = 0. \quad (31)$$

If these conditions were simultaneously fulfilled for all pairs of spins, a null vector independent of the actual values of k_{ij} and k'_{ij} would have been found. Postulating that conditions of the form of Eq. (31) exist for any pair of spins i and j suggests furthermore that the associated $\hat{\rho}_x$ has to be symmetric to permutations of the indices, i.e., no pair of indices must be special. This implies that all coefficients x_{ℓ} of $\hat{\rho}_x$ related to products of m \hat{P}_S terms ought to be identical in the steady state. Once this condition is applied, $\hat{K}'_{ij} \hat{\rho}_x = 0$ is always fulfilled, as the non-zero contributions from applying \hat{K}'_{ij} cancel

in pairs. For example, $\hat{K}'_{1,2}\hat{P}_S^{(1,3)} = -\hat{K}'_{1,2}\hat{P}_S^{(2,3)}$ and $\hat{K}'_{1,2}\hat{P}_S^{(1,3)}\hat{P}_S^{(2,4)} = -\hat{K}'_{1,2}\hat{P}_S^{(1,4)}\hat{P}_S^{(2,3)}$ follow from Eqs. (19) and (20) and the definition of \hat{K}'_{ij} [Eq. (4)], which implies $\hat{K}'_{ij}\hat{p}_x = 0$ for any linear combination of the basis operators employing the same coefficients for all operators of the same \hat{P}_S -multiplicity. Thus, $\hat{K}'_{ij}\hat{p}_x = 0$ alone specifies \hat{p}_x in this general setting. Indeed, in combination with the permutation symmetry, any particular condition of this form, e.g., $\hat{K}'_{1,2}\hat{p}_x = 0$, allows us to evaluate the sought null vector. A constructive proof of the existence of this symmetrized null vector is provided in the [supplementary material](#). This null vector is commensurable with the most general reaction network. Specific reaction networks may have larger null spaces, but the vector obtained above has to be contained within the null space. This is so because it applies to the most general reaction network, which contains any specific n -member reaction network by fixing the rate constants, possibly equating selected rate constants to zero. As long as the reaction network has a one-dimensional null space, the null vector established above fully specifies the steady state, i.e., $\hat{p}_\infty \propto \hat{p}_x$. This steady state is then unique and independent of the initial condition except for scaling. A detailed study of the coefficient matrices for $n = 3$ and $n = 4$ indicates that for these systems, the nullity is actually 1, independent of the choice of the k_{ij} 's except for if the reaction network is reducible, i.e., if the system can be decomposed into smaller, independent spin clusters (each with its own null space). This leads us to the somewhat surprising proposition that the steady state depends only on the number of reacting spins—and the initial condition in terms of scaling—and is independent of the details of the reaction network as long as the graph of reaction-coupled spins is irreducible. In the [supplementary material](#), we show that this is a general feature of irreducible reaction networks. Specifically, we demonstrate that adding an unreactive radical to an irreducible $(n - 1)$ -spin system yields a two-dimensional kernel. Upon introducing a single reaction (or multiple reactions) between the reactive and initially unreactive spins, the kernel is contracted to the single

null vector introduced above. Building up the reactive system in this way starting from two radicals, we observe that any reaction network that is described as a tree of order n (or is more densely coupled) exhibits a one-dimensional kernel, which gives rise to the described steady-state behavior. See the [supplementary material](#) for a detailed derivation.

c_1 is coupled to the coefficients related to the higher terms by necessarily non-zero entries, i.e., the rate constants, in **A**. Consequently, the null vector, if it exists, has to have a non-zero component corresponding to the $\hat{1}$ operator. Furthermore, as c_1 is constant [cf. Eq. (25)], the weight of the null vector in \hat{p}_∞ is entirely determined from the initial condition. Let us assume a radical pair, without loss of generality assigned to indices (1,2), in an environment of $(n - 2)$ random spins. We adopt the following initial condition parameterized by s_0 , the initial singlet probability of the spin-correlated pair:

$$\begin{aligned} \hat{p}(0) &= \frac{1}{2^{n-2}} \left(s_0 \hat{P}_S^{(1,2)} + \frac{1}{3} (1 - s_0) \hat{P}_T^{(1,2)} \right) \\ &= \frac{1}{2^{n-2} 3} \left((1 - s_0) \hat{1} + (4s_0 - 1) \hat{P}_S^{(1,2)} \right). \end{aligned} \quad (32)$$

Equation (32) includes the random initial configuration ($\hat{p}(0) = \hat{p}_0^{(F)} \propto \hat{1}$) for $s_0 = 1/4$ and the radical pair generated as singlet and triplet in an environment of random spins for $s_0 = 1$ and $s_0 = 0$, respectively. Expressing \hat{p}_∞ as a multiple of the (unique) null vector, we can conclude that

$$\hat{p}_\infty(s_0) = \frac{4}{3} (1 - s_0) \hat{p}_\infty^{(F)}, \quad (33)$$

where $\hat{p}_\infty^{(F)} = \hat{p}_\infty(s_0 = 1/4)$ is the steady-state spin density operator of the completely random initial configuration, $\hat{p}_0^{(F)}$. Equation (33) predicts a linear scaling of the survival probability with s_0 . Importantly, if one spin pair is initially in the singlet state ($s_0 = 1$), the

TABLE I. Steady-state survival probability, $p^{(F)}$, and density operator, $\hat{p}_\infty^{(F)}$, of irreducible F-clusters of size n . d is the number of operators in the operator basis given by Eq. (21). The multiplier of $\hat{1}$ is 2^{-n} and that of $\hat{W}_1^{(n)}$ is $-1/(2^{n-1}n)$. See the [supplementary material](#) for a derivation.

n	d	$p^{(F)}$	$\hat{p}_\infty^{(F)}$
2	2	$\frac{3}{4}$	$\frac{1}{4} \hat{1} - \frac{1}{4} \hat{P}_S^{(1,2)} = \frac{1}{4} \hat{1} - \frac{1}{4} \hat{W}_1^{(2)}$
3	4	$\frac{1}{2}$	$\frac{1}{8} \hat{1} - \frac{1}{12} \hat{W}_1^{(3)}$
4	10	$\frac{5}{16}$	$\frac{1}{16} \hat{1} - \frac{1}{32} \hat{W}_1^{(4)} + \frac{1}{48} \hat{W}_2^{(4)}$
5	26	$\frac{3}{16}$	$\frac{1}{32} \hat{1} - \frac{1}{80} \hat{W}_1^{(5)} + \frac{1}{160} \hat{W}_2^{(5)}$
6	76	$\frac{7}{64}$	$\frac{1}{64} \hat{1} - \frac{1}{192} \hat{W}_1^{(6)} + \frac{1}{480} \hat{W}_2^{(6)} - \frac{1}{960} \hat{W}_3^{(6)}$
7	232	$\frac{1}{16}$	$\frac{1}{128} \hat{1} - \frac{1}{448} \hat{W}_1^{(7)} + \frac{1}{1344} \hat{W}_2^{(7)} - \frac{1}{3360} \hat{W}_3^{(7)}$
8	764	$\frac{9}{256}$	$\frac{1}{256} \hat{1} - \frac{1}{1024} \hat{W}_1^{(8)} + \frac{1}{3584} \hat{W}_2^{(8)} - \frac{1}{10752} \hat{W}_3^{(8)} + \frac{1}{26880} \hat{W}_4^{(8)}$
9	2620	$\frac{5}{256}$	$\frac{1}{512} \hat{1} - \frac{1}{2304} \hat{W}_1^{(9)} + \frac{1}{9216} \hat{W}_2^{(9)} - \frac{1}{32256} \hat{W}_3^{(9)} + \frac{1}{96768} \hat{W}_4^{(9)}$
10	9496	$\frac{11}{1024}$	$\frac{1}{1024} \hat{1} - \frac{1}{5120} \hat{W}_1^{(10)} + \frac{1}{23040} \hat{W}_2^{(10)} - \frac{1}{92160} \hat{W}_3^{(10)} + \frac{1}{322560} \hat{W}_4^{(10)} - \frac{1}{967680} \hat{W}_5^{(10)}$

survival probability of the irreducible n -radical system will tend to zero, even if the initially generated singlet pair is unreactive, i.e., $k_{1,2} = 0$ (but coupled to the reaction network). If $s_0 < 1$, a fraction of the radical pair system will always survive for $t \rightarrow \infty$.

Following the approach outlined above, we have evaluated the steady-state density operator for connected reaction networks of up to $n = 10$ spins. Table I summarizes our results for the random initial condition; the supplementary material provides details of the construction of the unique null vector, which leads to these results. For conciseness, we denote the sum of all basis terms involving products of m orthogonal, singlet projection operators as $\hat{W}_m^{(n)}$,

$$\hat{W}_m^{(n)} = \sum_{\text{unique combinations}} \prod_p^m \hat{P}_S^{(i_p, j_p)}.$$

Using $\text{Tr}[\hat{P}_S^{(ij)} \hat{\rho}] = \text{Tr}[\hat{P}_S^{(ij)} \hat{\rho} \hat{P}_S^{(ij)}]$ and Eqs. (20), the survival probability of the spin cluster, p , and the singlet probability of any pairs of spins, $p_S^{(ij)}$, can be easily evaluated. For the random initial state, p is summarized in Table I. For a spin-correlated initial state of the form given by Eq. (32), $p(s_0)$ follows from Eq. (33), i.e.,

$$p(s_0) = \frac{4}{3}(1 - s_0)p^{(F)}, \quad (34)$$

where $p^{(F)} = p(s_0 = 1/4)$. In general, the survival probabilities decrease with increasing n . The singlet probability in the steady states is zero for any pair of spins, again independent of the topology of the (connected) reaction network and whether the spins are directly connected by a reaction.

V. MORE RESULTS AND DISCUSSION

We have demonstrated how spin effects of recombining n -radical systems can be rigorously described. Our analysis has provided a transparent interpretation of results that are intuitive and results that are surprising. As one would assume, the pairs of mutually reacting spins that survive the recombination event are triplet polarized. However, this principle appears to apply to any pair of spins of the reactive network, even those that are not directly reacting with each other. It is furthermore surprising that the spin state realized in the surviving spin system in the long-time limit is independent of the reaction topology of the network and the actual values of the rate constants as long as all spins are members of one reaction network. This steady state is directly correlated with the weight of the identity operator, i.e., the operator representing random encounters, in the initial state expressed in terms of the basis operators. This leads to another unanticipated realization: a singlet initial state will result in the complete decay of the n -spin cluster, again independent of the reaction topology even if the associated spin pair itself is not reactive. This “propagation of singlet spin correlation,” or “spin crystallization,” effect has earlier been implied for specific systems by Green and co-workers but here emerges as a general feature of coupled reaction networks.^{21,22} Note also that the intransigency of the steady state (in terms of being proportional to a well-defined null vector independent of reaction

details) does not imply that the dynamics that lead to this steady state or the reaction yields realized (for any time and the limit $t \rightarrow \infty$) are independent of the details of the reaction network.

A. Overall reaction yields

The overall reaction yield can be calculated by considering the n radical system and all $n - 2, n - 4, \dots$ sister radical systems that originate from the n -radical system by recombination of pairs of spins. In particular, recombination of pair (i, j) , e.g., gives rise to the $(n - 2)$ spin system, obeying the equation of motion

$$\frac{d\hat{\rho}_{(ij)}^{(n-2)}(t)}{dt} = \text{Tr}_{(ij)}[\hat{K}_{ij}\hat{\rho}^{(n)}(t)] - \sum_{a,b \notin \{i,j\}} \hat{K}_{a,b}\hat{\rho}_{(ij)}^{(n-2)}(t). \quad (35)$$

Here, $\hat{\rho}_{(ij)}^{(n-2)}(t)$ is understood to be defined in the Hilbert space of the spins $\{1, 2, \dots, n\} \setminus \{i, j\}$. For every pair of recombining spins, an equation of this form applies. As the equation of motion is linear, essentially identical subsystems that result along different recombination paths of the reaction network can be treated independently. The reaction product yields, which can easily be calculated by evaluating the dynamics of all coupled systems in the suggested operator basis, depend on the actual rate constants and the network topology. For a linear chain of $n = 3$ initially uncorrelated radicals recombining in the singlet state with the same rate constant k , a simple calculation using the Laplace transformed equations of motion and the final value theorem shows that 1/2 of the population will remain as a triplet-polarized three-spin system with the density matrix given by Eq. (29), while 1/4 of each will remain as the $n - 2 = 1$ radical system comprising only one of the terminal radicals. Instead, if all radicals can react with each other (triangular topology) with the same rate constant, the surviving, triplet-polarized $n = 3$ state is unaltered, but all three different single radical states are generated with an equal weight of 1/6. For $n = 4$, let us consider three scenarios of initially uncorrelated spins: the mutual reaction of all six pairs of spins, the square/ring topology, and the linear chain. In all cases, the survival probability of the $n = 4$ spin system approaches 5/16; the resulting states are given in Table 1. In addition, $n = 2$ radical systems survive the recombination event. For the linear chain, the two triplet-polarized pairs of terminal spins are (1, 2) or (3, 4), produced with probability 3/16 each, and an uncorrelated pair of spins 1 and 4 ($p_S^{(1,4)}/p = 1/4$), generated with probability 1/4. All spins recombine in the 1/16th fraction of the cases. For the square and densely coupled system, on the other hand, the surviving two-spin systems are always triplet polarized, involve any pair of the reacting four and six pairs, and occur with the probability of 9/64 and 3/32, respectively. For both cases, the total survival probability of a two-spin configuration is 9/16; a fraction of 1/8 recombines completely ($n = 0$). Figure 1 summarizes the survival probabilities of the $n' \leq n$ spin systems resulting from the random encounter of n spins for which all pairwise recombination processes occur at the same rate. It is interesting to note that while the expected number of surviving radicals increases from 3/2 to 1067/256 ≈ 4.2 for $n = 2$ to $n = 10$, the radical yield per radical input is largest for $n = 2$. It decreases from 3/4 for $n = 2$ to 1067/2560 ≈ 0.42 for $n = 10$. Thus, at least for these configurations, encounter pairs are, in principle, more efficient to yield triplet-polarized radicals.

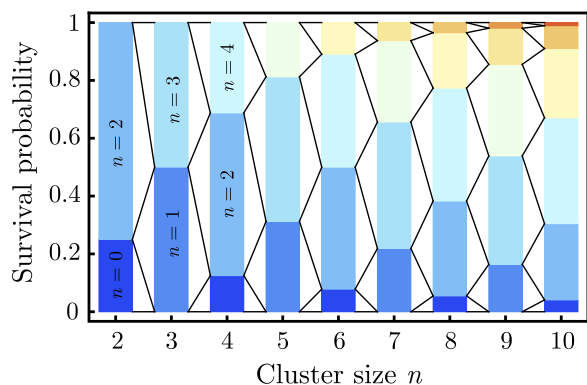


FIG. 1. Survival probabilities, p , of the $n' \leq n$ spin configurations resulting from n -spin clusters with random initial configuration (“F-clusters”) and an equal recombination rate constant of all pairs of spins. The bars give the cumulative survival probability of the n' spin systems starting with $n' = 0$ at the bottom. For odd (even) n , only spin systems with odd (even) n' are populated.

ST-dephasing does not alter the steady-state results for the linear and symmetric spin system with $n = 3$ spin and equal rates. For $n = 4$, the steady-state survival probability is independent of ST-dephasing for the symmetric ring and the all-to-all topology. However, for the linear four-spin chain, ST-dephasing alters the steady-state survival and singlet probabilities of the ensuing two-spin system comprising spins 1 and 4 and the probability of complete recombination, which become dependent on the rate

constant of ST-dephasing. For $k'_{ij} = k_{ij}/2 = k/2$, we find that for the (1,4)-two-radical system, $p = 59/240$ (vs $1/4$ for $k' = 0$) and $p_S^{(1,4)} = 7/120$ (vs $1/16$ for $k' = 0$), i.e., the additional dephasing slightly increases the triplet probability in this pair (to $14/59$ instead of the random $1/4$). For the totally symmetric all-to-all spin systems, the entire kinetics turn out to be independent of the ST-dephasing rate constant k' . For the other systems mentioned, the kinetics leading to the steady states are altered even if the steady states are not impacted by the dephasing process. Figure 2 illustrates the dependence of the recombination kinetics in linear $n = 3$ and $n = 4$ spin systems on the ST-dephasing rate (ranging from 0 to ∞). The pronounced effect of the ST-dephasing is in line with a previous suggestion to use radical triads to experimentally discriminate the Haberkorn and Jones–Hore approaches to spin-selective recombination.⁴⁰ However, only for the $n = 4$ system, this is reflected in the steady-state yield.

B. Radical scavenging for $n = 3$

The dynamics of radical systems undergoing spin-selective recombination reactions can be remarkably complex. A particularly intriguing aspect of this kind is the “chemical Zeno effect” as described by Letuta and Berdinskii.²⁴ The essence of this effect is that spin-selective recombination reactions of a member of a radical pair with a third, independent radical can drive singlet–triplet interconversions in the radical pair alone, i.e., even in the absence of coherent interconversion pathways (e.g., hyperfine interactions). In certain scenarios relevant to the avian compass model, the effect can be utilized to enhance the directional response to the geomagnetic field, and it provides a feasible pathway to accommodate quickly

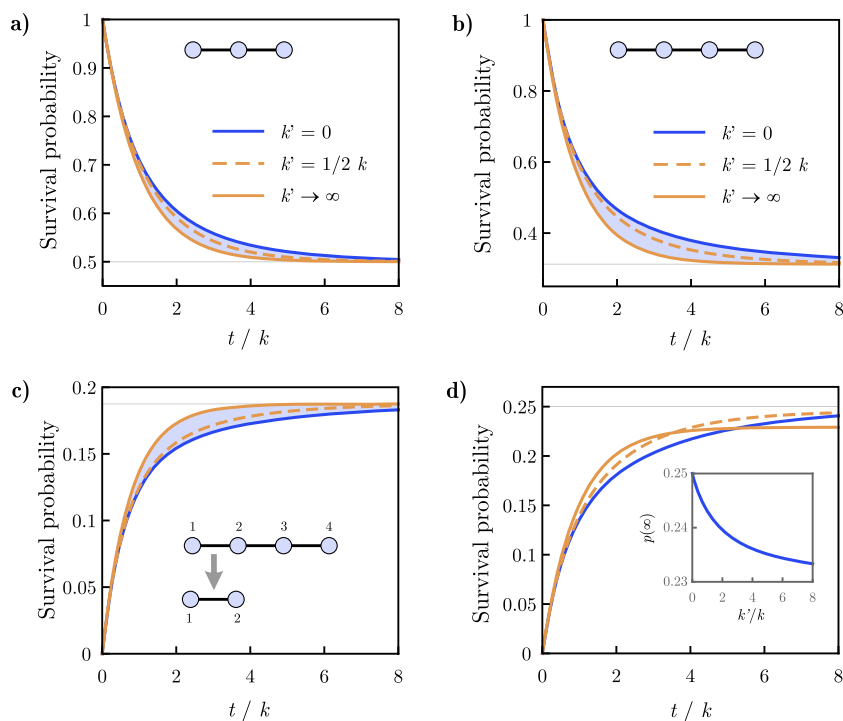


FIG. 2. Time-dependent survival probabilities, $p(t)$, of spin configurations resulting from linear three- and four-spin systems with a random initial state and equal recombination/ST-dephasing rate constants of adjacent spins. (a) and (b) Populations of the initial three-radical state or four-radical state of the spin chains. (c) and (d) Population of the radical pair states resulting from recombination of the linear spin chain with $n = 4$. (c) and (d) give the population of the terminal (1,2) radical pair and the central (2,3) radical pair, respectively. The inset of (d) illustrates the steady-state survival probability as a function of k'/k . The legends from (a) and (b) apply throughout. The analytical results underpinning these plots are provided in the [supplementary material](#).

relaxing species, such as superoxide, which would not elicit low-field magnetosensitivity in the RPM.^{25,26} Letuta and Berdinskii used a simple model to introduce the effect: a triplet-born radical pair, one radical of which exclusively reacts with an initially uncorrelated third radical. Assigning the radical pair to indices 1 and 2 and the radical scavenger to index 3, in the nomenclature of this manuscript, this corresponds to $\hat{p}(0) = \hat{p}_T^{(1,2)}/6$, $k_{2,3} \neq 0$, while $k_{i,j} = 0$ for all other pairs, including the (1,2) pair. This kinetic network is reducible, and unlike the scenarios discussed above, the kernel of **A** has dimension two (cf. the [supplementary material](#)). When the results of [Table I](#) do not apply, we can still use the outlined approach to construct **A** and solve [Eq. \(24\)](#) for the steady state. Using an initial condition of the form of [Eq. \(32\)](#), we find

$$\hat{p}_\infty = \frac{1-s_0}{6} \hat{1} + \frac{4s_0-1}{12} (\hat{p}_S^{(1,2)} + \hat{p}_S^{(1,3)}) - \frac{1}{8} \hat{p}_S^{(2,3)}. \quad (36)$$

This \hat{p}_∞ corresponds to a survival probability of 3/4 (independent of s_0) and a survived, singlet probability of

$$\frac{p_S^{(1,2)}}{p} = \frac{1}{12}(1+8s_0), \quad (37)$$

which is smaller (larger) than $s_0 = p_S^{(1,2)}(t=0)$ for $s_0 > 1/4$ ($s_0 < 1/4$), indicative of the induced singlet–triplet conversion. In view of the analysis carried out above, it becomes apparent though that this scenario is special insofar as the presence of any other reaction, radical pair recombination or simultaneous scavenging of

both radicals, even if present at a slow rate, changes the steady-state outcome to one of all radical pairs being triplet polarized and a lower survival probability as indicated in [Table I](#).

[Figure 3](#) summarizes the effect of a non-zero $k_{1,2}$ for different initial states; the underlying analytical results are summarized in the [supplementary material](#). For a singlet initial state of radical pair (1,2), additional reaction channels have the effect of accelerating the reaction-induced singlet–triplet interconversion and obliterating the survival of the system. For the triplet initial state, the singlet probability is initially attenuated and eventually reduced to zero, while the survival is only reduced by a little. If the system is short-lived and the radical recombination $k_{1,2}$ is slow, the behavior is still in qualitative agreement with the original description, i.e., the $k_{1,2} = 0$ limit. In addition, note that the transient effects will still reflect in the reaction yields if the radical system undergoes a competing reaction, e.g., spin-independent decay. Then, in combination with coherent evolution, a rich array of phenomena can still be expected for $k_{1,2} \neq 0$, despite the very uniform, even dull, steady state given by [Eq. \(29\)](#). Finally, we also note that the steady-state results in [Eqs. \(36\)](#) and [\(37\)](#) are independent of the ST-dephasing rate in the (2,3)-radical pair. This also applies for the decay of the three-radical population. Yet, the kinetics of the singlet probability are strongly influenced by $k_{2,3}$, as shown in [Fig. 4](#).

C. Radical scavenging for $n = 4$

The approach outlined here allows for a straightforward treatment of n -spin chemical Zeno scenarios. For an unreactive radical pair [spin indices (1,2)] scavenged by two initially uncorrelated radicals, the singlet–triplet interconversion yield in the pair

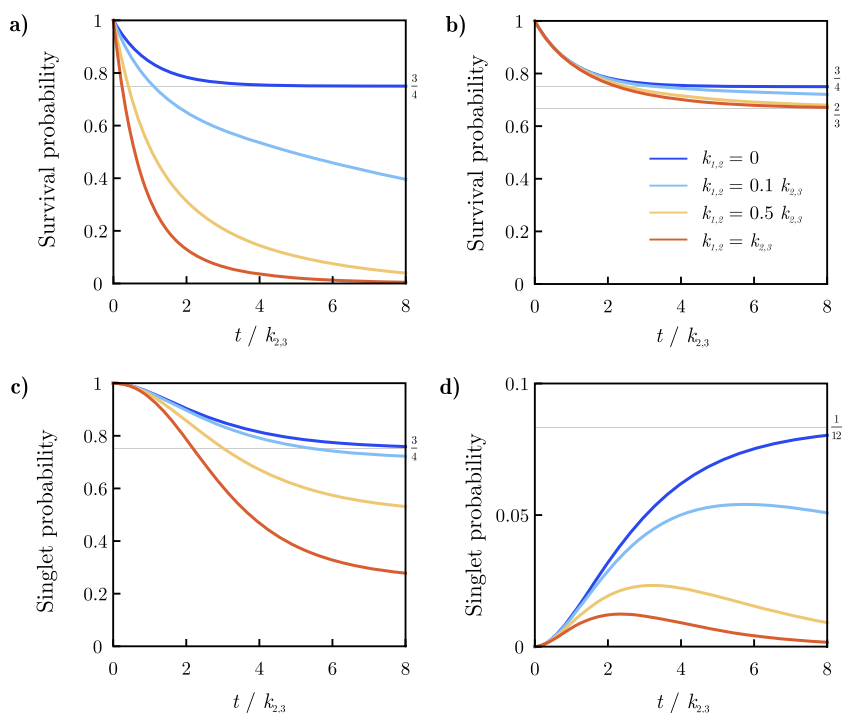


FIG. 3. Time-dependent survival probabilities, $p(t)$ (a) and (b), and singlet fractions of the survived population, $p_S^{(1,2)}(t)/p(t)$ (c) and (d), of a radical pair [(1,2)] born as singlet (a) and (c) or triplet (b) and (d) in the presence of a radical scavenger reacting with radical 2 in the singlet state with the rate $k_{2,3}$. The colors indicate different recombination rate constants in the (1,2)-pair, as summarized in the legend for (b). $k_{1,2} = 0$ is the classical “chemical Zeno”-scenario from [Ref. 24](#).

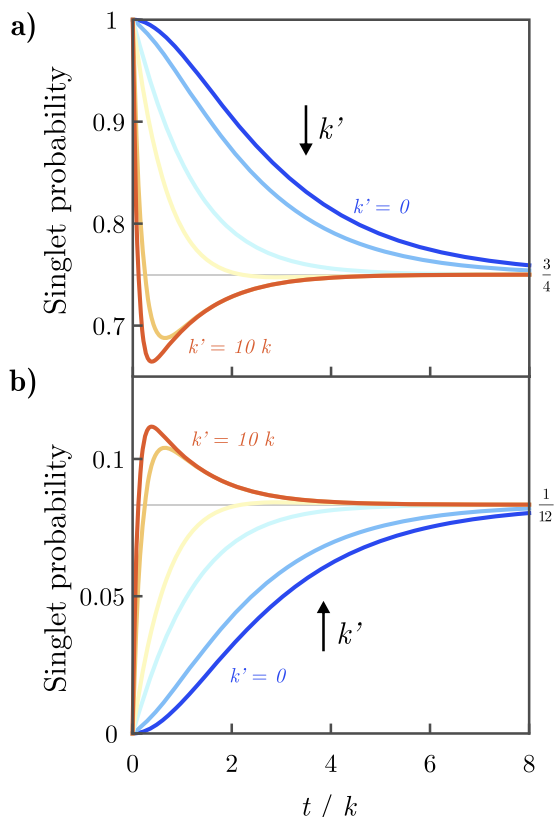


FIG. 4. Time-dependence of the singlet fractions of the survived population, $p_S^{(1,2)}(t)/p(t)$, of a radical pair $[(1,2)]$, born as (a) singlet or (b) triplet in the presence of a radical scavenger reacting with radical 2 in the singlet state with rate constant $k_{2,3} = k$ for various $k'_{2,3} = k' \in \{0, k/10, k/2, k, 5k, 10k\}$.

$(1,2)$ exceeds that induced by the three-spin chemical Zeno effect. Figure 5 illustrates the reaction-induced spin conversion in 4-radical systems (analytical results are summarized in the [supplementary material](#)). For a singlet-born radical pair, if one of the radicals is scavenged by radicals 3 and 4 (with the same rate constant, blue lines), $p_S^{(1,2)}$ is $1/3$. The same limiting singlet probability is obtained if the scavengers, in addition, react with each other; however, the limit is reached faster (light blue lines). The scenario of each of the radicals of $(1,2)$ reacting with one of the scavengers is hardly distinguishable from the former—yet, the long-time limit is slightly different with $p_S^{(1,2)} = 21/64$ (orange lines). Eventually, if, in addition to pairs $(1,2)$ and $(2,4)$, the scavenger pair $(3,4)$ is reactive, the reaction network is again connected, the kernel has nullity 1, and the steady state is reached with $p_S^{(1,2)} = 0$, in line with the description from above (see [Table I](#), red lines).

D. Consequences for magnetic field effects

The recombination in networks of radicals as described here could also have surprising consequences on the observed magnetic

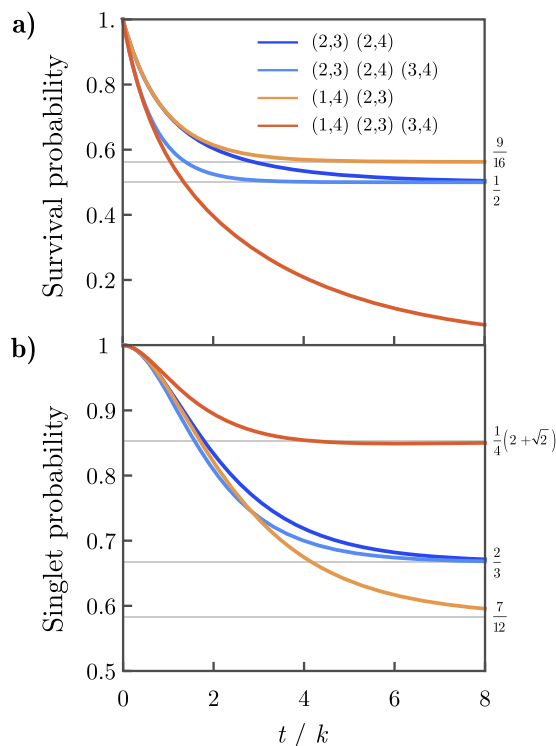


FIG. 5. Time-dependence of the survival probability, $p(t)$, and the singlet fractions of the survived population, $p_S^{(1,2)}(t)/p(t)$, of a radical pair $[(1,2)]$ born in the presence of two radical scavengers reacting with the radicals of the $(1,2)$ pair in the singlet state. The recombination rate constants between pairs of spins, as indicated in the legend, have been set equal to k ; pairs not explicitly stated are assumed unreactive. The underlying analytical results are summarized in the [supplementary material](#).

field effect, not only due to the effects discussed above but even on a simpler level. If radicals encounter at random, $1/4$ of the pairs will meet in the singlet configuration. Assuming that these pairs efficiently recombine forming a singlet product, as is often the case, the majority of the singlet encounters will immediately lead to product formation in a magnetic field independent manner. The remaining $3/4$ that meet as triplets are potentially susceptible to the influence of an applied magnetic field.¹⁰ Yet, the size of the relative magnetic field effects on the recombination product is limited by the field independent recombination of $1/4$ of the population in the first encounter. If we assume, on the other hand, that the recombining radicals prior to their encounter interact with a radical scavenger or a reactive network of radicals, e.g., as the result of being produced in temporospatial vicinity, the pairs of radicals surviving the initial recombination stage will be fully triplet polarized upon a subsequent encounter even if they did not directly encounter and potentially react with their partner radical. In principle, this enhanced triplet population of the encounter pair could subsequently give rise to larger relative magnetic field effects that exceed those resulting from comparable F-pair encounters.

VI. CONCLUSIONS

We have provided a rigorous description of the recombination kinetics of n radicals. This has been realized by determining an operator basis that comprises the initial state and is closed under the action of the phenomenological Haberkorn recombination superoperator and the ST-dephasing superoperator. The recoupling properties of spins form such a basis in the form of all singlet projection operators, and their products not involving any spin index more than once, augmented by the identity operator. This model can be used to predict the outcome of encounters of n radicals when coherent interconversion processes and spin relaxation are irrelevant or slow on the timescale of the recombination. In particular, it allows the evaluation of survival probabilities and spin correlation resulting from highly reactive “F-clusters,” the logical extension of F-pairs to $n > 2$ radicals. In this paper, we have used a description in terms of fixed rate constants, but a generalization to diffusion-modulated processes is obvious, in principle.

The recombination of clusters of radicals can produce spin-correlated states, which could form the starting point of spin-dependent processes and magnetic field effects. This could be due to the RPM or due to the electron–electron dipolar coupling, as suggested in the context of the DnM ,^{12,13} on a slower timescale. Surprisingly, we found that the spin-correlated state that is eventually realized in the surviving n -radical systems in the long-time limit is independent of the details of the reaction network, e.g., the specific rate constants and topology of reactive interactions, provided that all radicals remain kinetically coupled. The survival probability is then only a function of the initial configuration. For an initial singlet state, the system is determined to recombine, even if the singlet pair is not intrinsically reactive. More predictably, the radicals surviving in the initial cluster are mutually triplet polarized.

The formalism allows the calculation of the yields and kinetics of the entire recombination process, including its sister systems comprising $n - 2$, $n - 4$, ... radicals. These details do, in general, depend on the reaction details, including the degree of ST-dephasing. For example, in the linear 4-spin chain, both the recombination dynamics and yields [of the surviving (1,4)-radical pair system] are impacted by the ST-dephasing rate constant. On the other hand, for the totally symmetric reaction network (every radical reacting with every other radical at the same rate), the steady-state yields and kinetics have been found to be independent of ST-dephasing.

We have used the approach to revisit the chemical Zeno effect, i.e., the spin dynamics induced in a spin-correlated radical pair due to scavenging with a third, initially uncorrelated radical. Generalizing the original description by allowing recombination in the initially correlated radical pair, we find that in the steady state, the extended reaction network expectedly gives way to the kind of kinetics described above for coupled reaction networks, i.e., strongly departing from the dynamics of the original description of the effect. In particular, for a singlet-born pair, the survival probability will tend to zero, despite the singlet–triplet conversion induced by the chemical Zeno effect. However, the reaction-induced singlet–triplet conversions are evident in the transients. If the system undergoes secondary reactions, e.g., a spin-independent conversion, these effects could still be seen in the reaction yields. We have also studied the chemical Zeno paradigm in systems of four radicals. Provided

that the nullity of the reaction system is larger than 1, similar reaction related singlet–triplet conversion can be observed, with details depending on the reaction topology. Analytical expressions have been provided for several simple scenarios.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for an existence proof of the symmetrized null vector of (irreducibly) reaction systems, a discussion of the nullity of the reaction operator, and additional analytical results.

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APPENDIX: DERIVATION OF EQS. (19) AND (20)

The proof of Eq. (19c) relies on the recoupling properties of three angular momenta, henceforth denoted as j_1 , j_2 , and j_3 . In particular, the two sets of states resulting from either first coupling j_1 and j_2 to j_{12} and next coupling j_{12} to the total angular momentum J , i.e., $|((j_1 j_2) j_{12} j_3) JM\rangle$, or first coupling j_2 and j_3 to j_{23} and next coupling j_{23} with j_1 to yield the total angular momentum J , i.e., $|j_1(j_2 j_3) j_{23} JM\rangle$, are related by⁴¹

$$|((j_1 j_2) j_{12} j_3) JM\rangle = \sum_{J_{23}} |j_1(j_2 j_3) j_{23} JM\rangle \times \langle(j_1(j_2 j_3) j_{23}) J | ((j_1 j_2) j_{12} j_3) J\rangle, \quad (\text{A1})$$

where the M -independent recoupling coefficient, $\langle(j_1(j_2 j_3) j_{23}) J | ((j_1 j_2) j_{12} j_3) J\rangle$, can be expressed in terms of a Wigner $6-j$ symbol

$$\langle(j_1(j_2 j_3) j_{23}) J | ((j_1 j_2) j_{12} j_3) J\rangle = \sqrt{(2j_{12} + 1)(2j_{23} + 1)} \times (-1)^{j_1 + j_2 + j_3 + J} \begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & J & j_{23} \end{Bmatrix}. \quad (\text{A2})$$

The $6-j$ symbol can be re-expressed as a sum over products of four Clebsch–Gordan coefficients.⁴¹ A similar expression relates $|((j_1 j_2) j_{12} j_3) JM\rangle$ and $|((j_1 j_3) j_{13} j_2) JM\rangle$. In what follows, as $j_1 = j_2 = j_3 = 1/2$, we will suppress the dependence on the individual j_i 's. We require the following coefficients:

$$\langle j_{23} = 0, J = 1/2 | j_{12} = 0, J = 1/2 \rangle = -\langle j_{13} = 0, J = 1/2 | j_{12} = 0, J = 1/2 \rangle = -\frac{1}{2} \quad (\text{A3})$$

and

$$\begin{aligned} \langle j_{23} = 0, J = 1/2 | j_{12} = 1, J = 1/2 \rangle &= \langle j_{13} = 0, J = 1/2 | j_{12} = 1, J = 1/2 \rangle \\ &= \frac{\sqrt{3}}{2}. \end{aligned} \quad (\text{A4})$$

Note that the coefficients in Eq. (A3) differ in sign, which can be traced back to the symmetry property $\langle j_1, m_1; j_2, m_2 | J, M \rangle = (-1)^{j_1 + j_2 - J} \langle j_2, m_2; j_1, m_1 | J, M \rangle$. For succinctness, let us first identify the indices i, j , and k in Eq. (19c) with 1, 2, and 3, respectively. The left-hand side of the equation is thus

$$\begin{aligned} \{ \hat{P}_S^{(1,2)}, \hat{P}_S^{(2,3)} \} &= \hat{P}_S^{(1,2)} \hat{P}_S^{(2,3)} + \hat{P}_S^{(2,3)} \hat{P}_S^{(1,2)} \\ &= \left(\sum_M |j_{12} = 0, J = 1/2, M\rangle \langle j_{12} = 0, J = 1/2, M| \right) \\ &\quad \times \left(\sum_{M'} |j_{23} = 0, J = 1/2, M'\rangle \langle j_{23} = 0, J = 1/2, M'| \right) \\ &\quad + h.c. \\ &= -\frac{1}{2} \sum_M |j_{12} = 0, J = 1/2, M\rangle \langle j_{23} = 0, J = 1/2, M| \\ &\quad + h.c., \end{aligned} \quad (\text{A5})$$

where *h.c.* stands for the Hermitian conjugate of the expression preceding it, and we have made use of Eq. (A3). For more than three spins, the sum over M has to be extended to cover all relevant quantum numbers of the remaining spins. We shall rewrite all states in terms of states with specified j_{12} as

$$\begin{aligned} |j_{23} = 0, J = 1/2, M\rangle &= -\frac{1}{2} |j_{12} = 0, J = 1/2, M\rangle \\ &\quad + \frac{\sqrt{3}}{2} |j_{12} = 1, J = 1/2, M\rangle, \end{aligned} \quad (\text{A6})$$

$$\begin{aligned} \hat{P}_S^{(1,2)} \hat{P}_S^{(2,3)} \hat{P}_S^{(1,2)} &= \sum_M |j_{12} = 0, J = 1/2, M\rangle \langle j_{12} = 0, J = 1/2 | j_{23} = 0, J = 1/2 \rangle \langle j_{23} = 0, J = 1/2 | j_{12} = 0, J = 1/2 \rangle \langle j_{12} = 0, J = 1/2, M| \\ &= | \langle j_{12} = 0, J = 1/2 | j_{23} = 0, J = 1/2 \rangle |^2 \sum_M |j_{12} = 0, J = 1/2, M\rangle \langle j_{12} = 0, J = 1/2, M| \\ &= \frac{1}{4} \hat{P}_S^{(1,2)}, \end{aligned} \quad (\text{A10})$$

which demonstrates the validity of Eq. (20c) for this set of indices. It applies in general, because the expression depends on the square of the recoupling coefficient and, thus, is independent of the order of the spin indices, which governs its sign.

In order to prove Eq. (19d), we proceed in an analogous fashion. In this case, we require the recoupling of four spins, which can be expressed in terms of a 9- j symbol as

$$\langle ((j_a j_b) j_{ab}, (j_c j_d) j_{cd}) J | ((j_a j_c) j_{ac}, (j_b j_d) j_{bd}) J \rangle = \sqrt{(2j_{ab} + 1)(2j_{cd} + 1)(2j_{ac} + 1)(2j_{bd} + 1)} \begin{Bmatrix} j_a & j_b & j_{ab} \\ j_c & j_d & j_{cd} \\ j_{ac} & j_{bd} & J \end{Bmatrix}. \quad (\text{A11})$$

Here, again, the sign of the recoupling coefficient will depend on the order of the labels. For indices (1, 2, 3, and 4), the right-hand side of Eq. (19d) can be evaluated as follows:

$$\begin{aligned} |j_{13} = 0, J = 1/2, M\rangle &= +\frac{1}{2} |j_{12} = 0, J = 1/2, M\rangle \\ &\quad + \frac{\sqrt{3}}{2} |j_{12} = 1, J = 1/2, M\rangle. \end{aligned} \quad (\text{A7})$$

Using the first expression, we obtain

$$\begin{aligned} \{ \hat{P}_S^{(1,2)}, \hat{P}_S^{(2,3)} \} &= \frac{1}{2} \hat{P}_S^{(1,2)} - \frac{\sqrt{3}}{4} \sum_M (|j_{12} = 0, J = 1/2, M\rangle \\ &\quad \times \langle j_{12} = 1, J = 1/2, M| + h.c.). \end{aligned} \quad (\text{A8})$$

Expanding $\hat{P}_S^{(1,3)}$ and $\hat{P}_S^{(2,3)}$ in a similar fashion in the j_{12} -states, one finds that

$$\begin{aligned} \frac{1}{2} (\hat{P}_S^{(2,3)} - \hat{P}_S^{(1,3)}) &= -\frac{\sqrt{3}}{4} \sum_M (|j_{12} = 0, J = 1/2, M\rangle \\ &\quad \times \langle j_{12} = 1, J = 1/2, M| + h.c.), \end{aligned} \quad (\text{A9})$$

which essentially results from the sign change in Eq. (A3), as a consequence of which the terms corresponding to projectors on the $j_{12} = 0$ and $j_{12} = 1$ states cancel when forming the difference, while the transition operators on the right-hand side add up. Combining Eqs. (A8) and (A9), the sought identity [Eq. (19c)] is found. It is easy to convince oneself of the fact that the result is independent of the permutation of indices 1, 2, and 3 and thus applies for any triple of indices, which completes the proof.

Along the same lines,

$$\begin{aligned} \{ \hat{P}_S^{(1,3)}, \hat{P}_S^{(1,2)} \hat{P}_S^{(3,4)} \} &= (|j_{12} = 0, j_{34} = 0, J = 0, M = 0\rangle \langle j_{12} = 0, j_{34} = 0, J = 0, M = 0|) \\ &\times \left(\sum_{J', M'} |j_{13} = 0, j_{24} = J', J', M'\rangle \langle j_{13} = 0, j_{24} = J', J', M'| \right) + h.c. \\ &= \frac{1}{2} \hat{P}_S^{(12)} \hat{P}_S^{(34)} + \left(\frac{\sqrt{3}}{4} |j_{12} = 0, j_{34} = 0, J = 0, M = 0\rangle \langle j_{12} = 1, j_{34} = 1, J = 0, M = 0| + h.c. \right), \end{aligned} \quad (\text{A12})$$

where we have used that

$$\begin{aligned} |j_{13} = 0, j_{24} = 0, J = 0, M = 0\rangle &= \frac{1}{2} |j_{12} = 0, j_{34} = 0, J = 0, M = 0\rangle \\ &+ \frac{\sqrt{3}}{2} |j_{12} = 1, j_{34} = 1, J = 0, M = 0\rangle. \end{aligned} \quad (\text{A13})$$

Note that $J = 0$ is realized either by combining $j_{12} = j_{34} = 0$ or $j_{12} = j_{34} = 1$. Together with

$$\begin{aligned} |j_{14} = 0, j_{23} = 0, J = 0, M = 0\rangle &= -\frac{1}{2} |j_{12} = 0, j_{34} = 0, J = 0, M = 0\rangle \\ &+ \frac{\sqrt{3}}{2} |j_{12} = 1, j_{34} = 1, J = 0, M = 0\rangle, \end{aligned} \quad (\text{A14})$$

Eq. (A12) allows us to finally show that Eq. (19d) holds, whereby we proceed in analogy to the approach used for three spins above but expand all terms in the basis with well-defined j_{12} and j_{34} . Equation (20d) can be derived in a similar fashion.

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#).

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