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MolSpin—Flexible and extensible general spin dynamics software

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ABSTRACT

Magnetic field effects have been measured in various processes involving radical pairs, and such magnetic field effects have provided the basis for a popular hypothesis of magnetoreception in migratory song birds. The spin dynamics of radical pairs exposed to radiofrequency radiation have also been associated with changes in the production of reactive oxygen species within a biological cell, an effect that is potentially harmful. In order to investigate such phenomena theoretically, one needs to employ complex computations which rely on solving stochastic differential equations, which may appear significantly different for slightly different problems relying on spin dynamics. To avoid creating a manifold of specialized tools for various spin chemistry problems, MolSpin has been crafted as general software to handle spin systems of varied complexity. In particular, it permits solving the Liouville-von Neumann equation to obtain the time-evolution of the spin density operator, calculate quantum yields, allows us to utilize semiclassical methods, enables calculation of energy levels in an arbitrary spin system, and predicts resonance frequencies. MolSpin is designed with a high emphasis on extensibility that makes it easy to implement new or extend existing functionality.

I. INTRODUCTION

Some chemical processes involving radicals or radical pairs, in particular, can be influenced by external magnetic fields such that the associated reaction yields become magnetic field dependent. Such magnetic field effects, for example, provide the foundation for the radical pair-based theory of avian magnetoreception1–4 and have been corroborated experimentally in model systems.3,8 Radical pairs have also been proposed to influence formation of reactive oxygen species inside biological cells when exposed to radiofrequency radiation.9,12 All of the aforementioned radical pair processes rely on the interaction of the spin of unpaired electrons with magnetic fields applied externally and created internally by the atomic constituents of the radicals involved. Magnetic field effects are, however, not limited to radical pairs as it has been shown how the presence of a third radical might drastically affect the spin dynamics of a multiradical system,13,14 and the use of nitrogen-vacancy centers in nanodiamonds as magnetic sensors demonstrates how spin interactions with external magnetic fields can play a role even without any radicals present.15 The description of the dynamical evolution of the spin systems in all of the aforementioned examples becomes very complex when one moves away from simple proof-of-concept model systems. Software packages to account for this complexity exist but tend to focus on calculation of, e.g., NMR or EPR spectra.16–19 Specific in-house solutions for radical pair systems exist in many research groups but are typically limited to the investigation of one specific phenomenon of interest.

This paper introduces the new software package named MolSpin, which is a virtual spin dynamics laboratory that permits exploration of arbitrary spin systems or any process involving spins, as, for example, those illustrated in Fig. 1. MolSpin is designed to be as general as possible, putting great emphasis on extensibility; it permits easy implementation of new algorithms once the standard features do not suffice. Here we argue specifically that extending MolSpin...
is much easier than writing a new script in, e.g., Matlab or Python. In contrast to other existing spin dynamics software packages, MolSpin is not limited to specific calculation types, such as solving the Liouville-von Neumann equation, but can support completely different tasks such as semiclassical simulations or calculation of energy levels and resonance frequencies in spin systems of varied complexity. A notable feature of MolSpin is the possibility of using trajectories for all input parameters, which, for example, allows us to specify complex time-dependencies of parameters such as spin-spin interaction tensors or external magnetic fields.

II. FEATURES

As MolSpin is designed with the capability to perform a manifold of spin chemical calculations, the feature description will focus on the ability to perform a range of specific tasks rather than an exhaustive list of all the technicalities; these are described in the user manual. The list of tasks presented in this section is far from being complete but represents the wealth of studies that can be performed using MolSpin. Note also that the tasks outlined below rely on the implemented feature set of MolSpin, which do not require any extensions of the software and can be used right away. All of the MolSpin input files used for the examples presented below can be found in the supplementary material.

A. Time-evolution of spin system ensembles

An essential task in spin dynamics is to simulate the time-evolution of a spin system, and this is easily done using MolSpin. A typical time-evolution task would require calculation of the time-dependence of certain expectation values, in particular, the expectation values of state projection operators.

The time-evolution of the spin density operator describing the spin system ensemble, \( \rho(t) \), is governed by the Liouville-von Neumann equation:

\[
\frac{d\rho}{dt} = -i\hbar [H, \rho] + \mathcal{A}(\rho). \tag{1}
\]

Here, \( H \) is the spin Hamiltonian and \( \mathcal{A} \) is the reaction superoperator that accounts for processes that transforms the spin system, such as the chemical reactions. Once \( \rho(t) \) is known, the expectation value of a projection operator, \( P_i \), is defined as

\[
p_i(t) = \text{Tr}(P_i \rho(t)), \tag{2}
\]

where \( P_i = |i\rangle\langle i| \) for some quantum state \( |i\rangle \). The quantity \( p_i(t) \) describes the probability of finding a spin system in the quantum state \( |i\rangle \) at time \( t \). The Hamiltonian is constructed from any number of single-spin or double-spin interactions, which have the form

\[
H_{SS,ij} = \mu_B g_i S_i \cdot \mathbf{A} F, \quad H_{DS,ij} = \mu_B g_i S_i S_j, \tag{3}
\]

where \( \mu_B \) is the Bohr magneton, while \( i \) and \( j \) are indices for the interacting spins. The \( g \)-tensors, \( g_i \) and \( g_j \), are specified for each spin in the MolSpin input file, while \( A \) and \( \alpha \) are constant tensor and scalar, respectively, that may be specified for each interaction. \( \mathbf{F} \) is a field vector that must additionally be specified for single-spin interactions. \( S_i \) and \( S_j \) are the spin operators. Note that MolSpin relies on a simple but elaborate input file format for specifying spins, interactions, reaction operators, and so on. Plenty of examples may be found in the supplementary material, which lists the input files for all task examples presented here; additional examples are provided on the MolSpin website: www.molspin.eu.

A simple radical pair with a single magnetic spin-1 nucleus was used to illustrate a time-evolution calculation in Fig. 2(a), which shows the time-evolution of expectation values \( p_i \), where \( i \) refers to the spin states \( |S\rangle, |T_s\rangle, |T_+\rangle, \) and \( |T_-\rangle \), i.e., the singlet state and three triplet states, respectively. The calculation shows the singlet-triplet interconversion enabled by the presence of the magnetic nucleus, which is modulated by the presence of a static magnetic field. An oscillating magnetic field may radically change the dynamics of a radical pair, as illustrated in Fig. 2(b).

B. Magnetic field effects

Spin systems can be affected by external magnetic fields, and processes involving spin dynamics may, therefore, in some cases depend on both the relative orientation of the spin system, as well as the strength of such external magnetic fields. When spin system processes can lead to a variety of different products, a common quantity of interest is the quantum yield, which describes the probability of a spin system to end up in a specific product state. For the generic radical pair in Fig. 3(a), the quantum yields \( \Phi_\alpha \) and \( \Phi_\beta \) predict the relative yields of the two chemical species that would be obtained in an experiment; it is these quantum yields that may depend on the external magnetic field vector.

The quantum yields of spin chemical processes are defined as

\[
\Phi_i = k_i \int_0^\infty \text{Tr}(P_i \rho(B, t)) \, dt. \tag{4}
\]

Here, \( k_i \) is the rate constant for the process \( i \), and \( P_i \) is the projection operator onto the quantum state \( |i\rangle \) that may participate in the
FIG. 2. Time evolution of a model spin system. The expectation values of the singlet and three triplet states were calculated for a simple radical pair model consisting of two unpaired electrons and a single spin-1 nucleus on the first radical. (a) A static $50 \mu T$ magnetic field in the $yz$-plane of the radical pair was applied at a $45^\circ$ angle relatively to the $z$ axis. (b) An additional magnetic field oscillating at $1.4$ MHz along the $z$-axis with an amplitude of $100 \mu T$ and $0$ phase was applied. The radical pair was initially produced in the singlet state, and no reaction superoperator was included here.

process (or the identity operator for spin-independent processes). The time-evolution of the density operator $\rho$ is given by Eq. (1); here, the density operator and hence the quantum yield also depend on the orientation and field strength of the external magnetic field, $B$. The index $i$ refers to a specific process, i.e., one would define quantum yields $\Phi_{P_1}(B)$ and $\Phi_{P_2}(B)$ in order to represent the processes shown in Fig. 3(a), where the projection operators $P_1$ and $P_2$ are the singlet and triplet projection operators, respectively. MolSpin contains a variety of methods for solving Eq. (4), relying on different assumptions to speed-up the calculations. The most general method is brute-force numerical integration using a leapfrog algorithm, while a faster method based on a Laplace-transformation may be used when there are no time-dependent interactions. The fastest method, specifically designed for calculations on radical pairs, furthermore assumes that no spin-dependent reactions are present as well as the assumption that no coupling exists between the two unpaired electrons of the radical pair such that each radical can be treated individually. All of these calculation methods rely on basic procedures such as diagonalization of the Hamiltonian or solving a linear system of equations. These functions are provided by the Armadillo library, which in turn relies on external high-speed math libraries to carry out the computations, such as OpenBLAS, Intel MKL, ARPACK, and LAPACK.

Radical pair processes such as those defined in Fig. 3(a) are thought to be responsible for endowing migratory song birds with their magnetic compass sense, where one could imagine that one of the reaction products, say $P_1$ from the singlet spin state, would produce the compass signal that would through some still-unknown means be perceived by the bird. It would, therefore, be relevant for magnetoreception to evaluate the singlet quantum yield as a function of orientation relative to the geomagnetic field in order to gauge the orientational dependence of the radical pair processes. The

FIG. 3. Magnetic field effects in a radical pair process. (a) A generic reaction scheme, where the radical pair is produced in the singlet state and interconversion between singlet and triplet states is possible. Different reactions may happen from the singlet and triplet states, leading to chemically distinct reaction products, and external magnetic fields may influence the singlet-triplet interconversion, thereby affecting the relative amount of reaction products, $\Phi_{P_1}$ and $\Phi_{P_2}$. (b) A calculation of the singlet quantum yield, $\Phi_{P_1}$, for the radical pair $[\text{FAD}^{++} \ldots \text{W}^{++}]$ in cryptochrome, shown in (c), including 14 magnetic nuclei. (c) The orientation of the external magnetic field is varied in the $xz$-plane of the molecular reference frame as defined on the isoalloxazine moeity of FAD$. The 14 magnetic nuclei included in the calculation are labeled.
putative magnetosensor radical pair of the avian magnetic compass is an [FAD$^*\ldots$W$^*$] radical pair hosted by the flavoprotein cryptochrome.\textsuperscript{1,4,30,37–40} A calculation of the singlet yield was performed recently,\textsuperscript{47} and here, the calculation has been repeated using MolSpin; the result is illustrated in Fig. 3(b). The main challenge posed by this calculation is the number of nuclear spins included; there are 11 spin-$\frac{1}{2}$ nuclei (protons) and 3 spin-1 nuclei (nitrogen atoms) in addition to the two electronic spins, distributed with 7 magnetic nuclei on each radical. It is possible to include more nuclear spins in such a calculation in MolSpin although the calculation time may become unreasonably long for a complete quantum mechanical description.

C. Reaction yield detected magnetic resonance (RYDMR)

The dynamics of spin systems can be affected by the oscillating magnetic field component of radiofrequency radiation, a property exploited to a large extent in the important experimental EPR and NMR techniques. Magnetic resonance effects due to radiation exposure, therefore, also have an effect on the quantum yields of spin chemical processes.

The presence of an oscillating magnetic field may affect the quantum yields defined in Eq. (4), such that the quantum yields depend on the amplitude, frequency, phase, and polarization of the oscillating magnetic field. In some very special cases of oscillating magnetic fields, the time-dependence of the spin system Hamiltonian can be removed by transforming it to a rotating reference frame,\textsuperscript{9,42} but normally one would have to deal with a time-dependent Hamiltonian when working with oscillating magnetic fields, and in such cases, Eqs. (1) and (4) can be solved by numerical integration. MolSpin uses a leapfrog algorithm with a constant time step for all currently implemented task classes relying on numerical integration.\textsuperscript{27} Note that the periodicity of the time-dependence for oscillating magnetic fields can be exploited to gain a significant performance boost for the calculations. In particular, the $\gamma$-COMPUTE algorithm\textsuperscript{43,44} which is implemented in MolSpin additionally averages the quantum yield over the phase of the oscillating magnetic field.

A change in the concentrations of reactive oxygen species, O$_2^*$ and H$_2$O$_2$, in particular, has been observed in certain cell types after exposure to radiofrequency radiation, and it was suggested that spin dynamics of a [FADH$^*\ldots$O$_2^*$] radical pair was responsible for the observed effects.\textsuperscript{11,12,45} Spin dynamics of this specific radical pair when exposed to radiofrequency radiation was explored using MolSpin as illustrated in Fig. 4, where the FADH$^*$ radical was simulated using 5 hyperfine interactions, while the superoxide radical was assumed to be in its most abundant form with nonmagnetic isotopes for the atomic nuclei. The simulation included a static magnetic field of 50 $\mu$T and a linearly polarized radiation field oscillating along an axis rotated by an angle $\theta$ relative to the static magnetic field with an amplitude of 2.8 $\mu$T. The simulation was done for 5 different values of the angle $\theta$.

The calculated singlet quantum yield was compared with the result of a simulation without the presence of the oscillating magnetic field, such that the quantum yield change could be obtained. Only a very small effect ($\lesssim 1\%$) is observed in Fig. 4 since the amplitude of the oscillating magnetic field is small, but note the largest magnitude for the quantum yield change is observed near 1.4 MHz which is the Larmor frequency for the unpaired electron in the O$_2^*$ superoxide radical. Often in realistic environments, the actual effect would be even smaller due to both spin-orbit coupling and spin relaxation caused by molecular motion,\textsuperscript{47} which were not included in this calculation.

**FIG. 4.** Reaction yield detected magnetic resonance in the [FADH$^*\ldots$O$_2^*$] radical pair. (a) The FADH$^*$ radical was simulated using 5 hyperfine interactions, while the superoxide radical has none. (b) The reference frame and 5 magnetic nuclei included in the calculation. A static magnetic field $B$ of 50 $\mu$T was placed along the z-axis, and an oscillating magnetic field $B$ at an angle $\theta$ relative to the static magnetic field was placed along the xz-plane; the five different curves in A correspond to different values of the angle $\theta$. The singlet yield calculation was compared to a calculation without the oscillating field in order to obtain the singlet yield change. The radical pair was produced in a mixed triplet state ensemble consisting of an equal amount of |T$_2$>, |T$^-$>, and |T$^+$>. The lifetime of the radical pair was assumed to be 1 $\mu$s; the hyperfine interactions and the reference frame were adopted from an earlier study.\textsuperscript{46}
D. Energy levels of spin systems

The dynamics of spin systems are governed by their spin Hamiltonians, which describe the energy of the spin system. The eigenvalues and eigenstates of the spin Hamiltonian define the energy levels of the system, and a spin system prepared in an energy eigenstate will remain unchanged over time insofar as it remains an eigenstate (i.e., if the spin Hamiltonian is time-independent). Most of the peculiarities observed in, e.g., RYDMR spectra or other magnetic field effects in the quantum yield can be explained in terms of transitions between the different energy levels of a spin system. It is, therefore, important to know these energy levels precisely.

Each energy level in a spin system consists of an eigenstate of the spin Hamiltonian and its associated eigenvalue, i.e.,

$$H(t)|n(t)\rangle = \varepsilon_n(t)|n(t)\rangle,$$

where $|n(t)\rangle$ and $\varepsilon_n(t)$ are the eigenstate and eigenvalue, respectively, for an energy level in the spin system at time instance $t$. Normally, one only considers the eigenvalue $\varepsilon_n(t)$ describing the energy, but MolSpin also offers a simple characterization of the energy level using state projection operators,

$$\langle P_i \rangle_n(t) = \langle n(t)|P_i|n(t)\rangle.$$

Here, $P_i$ is a chosen projection operator onto any state $|i\rangle$, such that $\langle P_i \rangle_n(t)$ is the expectation value of the projection onto state $i$ calculated from eigenstate $|n(t)\rangle$. In other words, $\langle P_i \rangle_n(t)$ measures similarity between the Hamiltonian eigenstate $|n(t)\rangle$ at time instance $t$ and a specified spin state $|i\rangle$.

The energy levels of the radical pair studied in Fig. 2 were calculated as an example, and the results are illustrated in Fig. 5. The spin-1 nucleus in the radical pair splits the energy levels into three groups, and it is seen in Fig. 3 how the $|T_+\rangle$ and $|T_-\rangle$ spin states within each group are directly influenced by the oscillating magnetic field at all times and transition into one another when the oscillating magnetic field changes sign. The singlet and $|T_0\rangle$ energy levels, on the other hand, remain nearly constant most of the time and only change slightly once the energy levels with $|T_+\rangle$ or $|T_-\rangle$ character gets close enough to mix the spin states.

E. Resonance frequency spectrum

Investigation of the effects of oscillating magnetic fields on the quantum yield easily becomes expensive computationally, and therefore, a much cheaper alternative in MolSpin is also available: the resonance frequencies can be calculated directly from the energy levels. The drawback of such a direct calculation of resonance frequencies is that it provides no information about the impact of each individual resonance frequency on the quantum yield, if any at all, but illustrates a set of possible frequencies that may have an effect on the spin system.

Each resonance frequency is defined using the difference between two energy level eigenvalues,

$$\nu_{ij} = \frac{|\varepsilon_i(t) - \varepsilon_j(t)|}{2\pi\hbar},$$

where $i$ and $j$ refer to the two different energy levels and a resonance frequency is calculated between each pair of energy levels. In addition, MolSpin can also calculate transition matrix elements for all of the transitions, which indicate the likelihood of radiation with a resonance frequency $\nu_{ij}$ to affect the spin system. The transition matrix elements are defined as

$$A_{ij} = \langle i|S_q|j\rangle, \quad A_{ij}^\dagger = \langle i|S_q^\dagger|j\rangle, \quad A_{ij}^\dagger = \langle i|S_q^\dagger|j\rangle.$$

Here, $S_x$, $S_y$, and $S_z$ are the spin operators for spin $q$, while $|i\rangle$ and $|j\rangle$ are the Hamiltonian eigenstates corresponding to the two energy levels. The transition matrix elements defined in Eq. (8) may be used to assess the relevance of the various resonance frequencies for the dynamics of the spin system.

The effect of radiation on the $\text{FADH}^+\cdots\text{O}_2^-$ radical pair was illustrated above through the simulation illustrated by Fig. 4, but a much cheaper analysis can be made by simply considering the resonance frequencies of the radical pair. The set of resonance frequencies calculated for the $\text{FADH}^+\cdots\text{O}_2^-$ radical pair model is...
shown as a histogram in Fig. 6(a); the figure shows that the radical pair has resonance frequencies almost as large as 90 MHz despite the singlet yield change is constantly close to zero above 4 MHz, as shown in Fig. 4. Part of this inconsistency between Figs. 4 and 6(a) can be explained through Fig. 6(b), which shows a spectrum $S_q(v)$ ($q = x, y, z$) defined as

$$S_q(v) = 1 - \prod_{i,j} (1 - \mathcal{P}_{ij} \cdot \mathcal{L}(v_\nu, v_j) \cdot \Delta v),$$

$$\mathcal{L}(v_\nu, v_j) = \frac{1}{\pi} \frac{y}{y^2 + (v - v_j)^2},$$

where $\mathcal{L}(v_\nu, v_j)$ is a Lorentzian lineshape function centered on a specific resonance frequency $v_j$ and with half-width at half-maximum given by the parameter $y$ and $\mathcal{P}_{ij}$ is the transition probability caused by a magnetic field oscillating along the axis $q = x, y, z$. Note that $\mathcal{P}_{ij} \cdot \mathcal{L}(v_\nu, v_j)$ is a probability density (in units of MHz$^{-1}$), which is turned into a probability by discretizing the frequency range and multiplying with the discretization step $\Delta v$. Thus, $1 - \prod_{i,j} (1 - \mathcal{P}_{ij} \cdot \mathcal{L}(v_\nu, v_j) \cdot \Delta v$ is the probability that the transition between energy levels $i$ and $j$ does not occur in the spin system when it is exposed to radiation within the frequency range ($v - \Delta v/2, v + \Delta v/2$), and the product in Eq. (9), therefore, describes the total probability that no transition occurs. The spectrum $S_q(v)$, therefore, describes the probability that a nonzero number of transitions occurs in the spin system, when it is exposed to radiation with a frequency in the range ($v - \Delta v/2, v + \Delta v/2$). It should be noted that this approach only considers first order excitations, and a more rigorous treatment should include higher order effects.

The individual transition probabilities for the radical pair are defined as

$$\mathcal{P}_{ij} = | \langle \delta S_{ij} + S_{ij} \rangle |^2 = |A_{ij,1x} + A_{ij,2z}|^2,$$

where $S_{1x}$ and $S_{2z}$ are the $S_i$ spin operators for the first and the second unpaired electrons of the radical pair, respectively; the transition probabilities for a magnetic field oscillating along the $y$ and $z$ axes, $\mathcal{P}_{ij, y}$ and $\mathcal{P}_{ij, z}$, are defined in a similar way.

Note that only few resonance frequencies from Fig. 6(a) contribute significantly to the spectrum shown in Fig. 6(b) due to low transition probabilities, and even the transitions with nonzero transition probability are not guaranteed to affect the quantum yield significantly. Still, Fig. 6(b) predicts a large resonance effect around a frequency of 1.4 MHz as is elaborated in Figs. 6(c) and 6(d); this prediction compares well with the prominent resonance seen around 1.4 MHz in Fig. 4, corresponding to the Larmor frequency of the superoxide radical, and notes how the effect is largest in Fig. 4 for an angle between the static and oscillating magnetic fields of around 90°, corresponding to an oscillating magnetic field along the $x$-axis rather than the $z$-axis, in agreement with the lower transition probability in Figs. 6(b) and 6(d) for magnetic fields oscillating along the $z$-axis compared to oscillations along the $x$- and $y$-axes.

![Fig. 6](https://example.com/image.png)

**Fig. 6.** Resonance frequencies of the [FADH$^+$→...O$_2^-$] radical pair. (a) The set of resonance frequencies can be visualized as a histogram. (b) A better representation of the resonance spectrum can be produced using Eq. (9) as it also takes the transition probabilities defined in Eq. (10) into account. The half-width at half-maximum parameter for the Lorentzian lineshape function was chosen as $y = 0.1$ MHz to produce narrow spectral lines, and 5000 data points were used to cover the interval from 0 MHz to 90 MHz, i.e., $\Delta v = 0.018$ MHz in order to properly resolve all spectral lines. (c) and (d) show the low-frequency part of the spectrum where the only peak with a significant transition probability is seen at 1.4 MHz, while the transition probability of all other peaks is well below 0.1, as seen in (b). The peak at 1.4 MHz is consistent with the largest singlet yield change in Fig. 4(a). The coordinate frame used for the calculation is defined in Fig. 4(b).
**F. Complex reaction schemes**

Spin dynamical processes may often be involved in complex systems, where a total reaction scheme would describe several products and intermediate states for the dynamical system. The reaction leading from one of the individual intermediate or product states to another could, for example, be an electron transfer process, and often the reactions are reversible. If multiple intermediate states exhibit spin dynamics, it would in some cases be relevant to simulate the full dynamics including the transitions between these states with active spin dynamics. All of the intermediate states in a reaction scheme with active spin dynamics may essentially be described as different systems; if a radical is transformed into another radical through an electron transfer process, for example, this new radical feels a different set of interactions as it resides in a different local molecular environment. Investigations relying on complex reaction schemes may, therefore, be described in terms of multiple spin systems which can be interconverted to one another through various reaction pathways such as electron transfers.

Simulations of multiple spin systems can be performed in two different ways in MolSpin, and in the description of these methods, it will be assumed for simplicity that there are only two spin systems, described by the density operators \( \rho_1 \) and \( \rho_2 \); generalization toward a more complex spin system then follows logically as discussed below. In the first approach, one enlarges the vector space such that it contains both Hilbert spaces, thereby including both density operators \( \rho_1 \) and \( \rho_2 \),

\[
\rho_i = \begin{pmatrix} \rho_{1i} & 0 \\ 0 & \rho_{2i} \end{pmatrix}, \quad H_i = \begin{pmatrix} H_{1i} & 0 \\ 0 & H_{2i} \end{pmatrix}. \tag{11}
\]

Here, \( \rho_i \) and \( H_i \) are the density operator and Hamiltonian of the enlarged vector space, respectively. The dynamics of the enlarged system is then described by the Liouville-von Neumann equation,

\[
\frac{d\rho_i}{dt} = -\frac{i}{\hbar} [H_i, \rho_i] + \mathcal{X}_i(\rho_i) + \mathcal{C}(\rho_i), \tag{12}
\]

where operator \( \mathcal{C} \) denotes the creation operator, while \( \mathcal{X}_1 \) and \( \mathcal{X}_2 \) are the reaction operators in the two spin systems as in Eq. (1). Without the creation operator, the two spin systems would still be completely independent in the enlarged vector space. The role of the creation operator, however, is to create transitions from one spin system to another. A transition between the two spin systems consists of two elements: (i) remove a part of one system and (ii) add a corresponding part to the other system. The reaction operators already take care of (i), so the role of a creation operator is essentially to add something to a spin system. If \( \rho_{1i} \) denotes a spin state in the first spin system and \( \rho_{2j} \) denotes a spin state in the second spin system, then the creation operator corresponding to the transition \( \rho_{1i} \rightarrow \rho_{2j} \) is defined as

\[
\mathcal{C}(\rho_i) = k[\rho_{2j}; \psi(\rho_{1i} \rho_{1j} \rho_{1o}) \rho_{2j} \psi] \tag{13}
\]

where \( k \) is the corresponding transition rate. Since the creation operator \( \mathcal{C} \) occupies an off-diagonal block in the enlarged vector space, the enlarged space is required in order to use this approach.

The other approach implemented in MolSpin which includes transitions between spin systems performs numerical integration using reaction operators with an opposite sign as the creation operators; here, an effective rate constant depends on the source spin system. It is therefore important to stress that no enlargement of the vector space is required using this approach as the creation operators are defined within the vector space where creation occurs. Assuming that Haberkorn reaction operators \( P_{1q} \) are used and that only a single transition from \( \rho_1 \) to \( \rho_2 \) exists, the Liouville-von Neumann equation for the two systems can be written as

\[
\begin{align*}
\frac{d\rho_1}{dt} &= -\frac{i}{\hbar} [H_1, \rho_1] - \frac{k}{2} (P_{1o} \rho_1), \\
\frac{d\rho_2}{dt} &= -\frac{i}{\hbar} [H_2, \rho_2] + k\alpha(t) \frac{P_{2o}}{\text{Tr}(P_{2o})},
\end{align*} \tag{14}
\]

where \( P_{1o} \) and \( P_{2o} \) are projection operators in the Hilbert spaces of \( \rho_1 \) and \( \rho_2 \), respectively. The subscripts \( q \) and \( r \) refer to the subspaces in the Hilbert spaces, such as the electronic triplet states in a radical pair. The notations \( P_{1q} \) and \( P_{2r} \), therefore, are subspace projections rather than projections onto a single state, which makes the approach much simpler to use than the enlarged vector space approach which only considers transitions between individual states of each spin system. The density removed from \( \rho_1 \) is just added to \( \rho_2 \); the important distinction from the traditional Haberkorn reaction operators is the dynamic effective rate "constant" \( k\alpha(t) = k \text{ Tr}(P_{1o}\rho_1(t)) \), where the trace \( \text{Tr}(P_{1o}\rho_1(t)) \) describes the probability that a sample from ensemble \( \rho_1 \) is found in the subspace where \( P_{1q} \) projects onto. Note that the formalism in Eq. (14) is equivalent to the enlarged vector space approach since \( \text{Tr}(P_{1o}\rho_1) = \rho_{1o} \rho_{1o} \rho_{1o} \) when only single states are considered, but the numerical algorithms are very different. The second method may include time-dependent interactions and scales much better than the enlarged vector space method; however, the enlarged vector space method is faster for small systems as it may use a larger integration time step.

The generalization of the formalism to handle more than two spin systems is perhaps most straightforward for the enlarged vector space approach, which just requires adding more diagonal blocks for \( \rho_{1p} \), \( \rho_{1q} \), etc., introducing \( H_3 \), \( H_4 \), etc. in Eq. (11) and similarly add more diagonal elements to the reaction operator in Eq. (12). The creation operators between different spin systems still follow Eq. (13). Generalizing the other approach is done by extending Eq. (14); note that the creation term with the effective rate constant is the only non-standard term in Eq. (14) and multiple terms with different effective rate constants would then be needed, i.e., one creation term for each transition between spin systems.

The radical pair hosted by an avian cryptochrome 4 protein displays a very complex reaction scheme. Initially, a radical pair \( \text{FAD}^+ \ldots \text{W}^+_\text{A} \) may be produced after photolysis of cryptochrome; here, FAD is a flavin adenine dinucleotide cofactor of the cryptochrome protein, and \( \text{W}^+_\text{A} \) is a nearby tryptophan amino acid. A secondary tryptophan residue, \( \text{W}^+_\text{B} \), may then transfer an electron leading to formation of the radical pair \( \text{FAD}^+ \ldots \text{W}^-\text{C}_{\text{B}} \), and this procedure is repeated twice more with two additional tryptophans to generate the radical pairs \( \text{FAD}^+ \ldots \text{W}^-\text{C}_{\text{B}} \) and \( \text{FAD}^+ \ldots \text{W}^-\text{C}_{\text{B}} \). The production of the radical pair \( \text{FAD}^+ \ldots \text{W}^-\text{C}_{\text{B}} \) happens on such a short time scale that no significant spin dynamics happens in the radical pairs involving \( \text{W}^+_\text{A} \) or \( \text{W}^+_\text{B} \), but the radical
pairs with $W_C$ and $W_D$ both possess a sufficiently long lifetime for appreciable spin dynamics to occur. Furthermore, it is assumed here that the unpaired electron of the tryptophan radical may jump back and forth between $W_C$ and $W_D$, such that a full description of the spin dynamics in cryptochrome should take both of these radical pair states into account.

A simulation of the collective spin dynamics of both radical pair states can be performed in MolSpin by treating $\lbrack \text{FAD}^\ast \cdots \cdot W^\ast_C \rbrack$ and $\lbrack \text{FAD}^\ast \cdots \cdot W^\ast_D \rbrack$ as two separate spin systems, with a transition between the two spin systems to account for the electron hopping back and forth, as illustrated by the reaction scheme shown in Fig. 7(a). For the sake of this example, a very simple model with a single nitrogen-nucleus on FAD as well as on both $W_C$ and $W_D$ has been assumed, with identical hyperfine interactions in the two tryptophans. The transition between the two spin systems conserves the spin state of the two electronic spins and the nitrogen nucleus on FAD but leads to a mixed ensemble of tryptophan nucleus spin states in order to account for the thermal fluctuations. Since the multiple spin systems approach effectively corresponds to a coupling to the thermal bath of the environment, it directly introduces spin relaxation in the total spin system, which affects the spin dynamics as illustrated in Figs. 7(c) and 7(d).

Setting up a simulation with both radical pair states may be quite involved when using the enlarged vector space approach as evidenced by the length of the MolSpin input file which may be found in the supplementary material. The input file defines two spin systems which both contain 4 spins: the two unpaired electrons, the N5 nucleus on FAD, and the N1 nucleus on a tryptophan. This means that there are 36 spin states in both spin systems, 9 singlet states and 27 triplet states, and the transitions between the spin systems must be specified one state at a time. Transitions from the singlet state $\lbrack W^\ast_C ; S, N5 = +1, N1 = +1 \rbrack$ in $W^\ast_C$, for example, into the states $\lbrack W^\ast_D ; S, N5 = +1, N1 = +1 \rbrack$, $\lbrack W^\ast_D ; S, N5 = +1, N1 = 0 \rbrack$, and $\lbrack W^\ast_D ; S, N5 = +1, N1 = -1 \rbrack$ were created with equal probability in order to randomize the tryptophan spin while conserving the spin of the electrons and FAD N5. Similar transitions were also created from all 35 other states, and the transitions from $W^\ast_D$ to $W^\ast_C$ were constructed in a similar way. Note that a more realistic calculation could be achieved by including the N1 nucleus of both tryptophans in both spin systems although such an approach would be less efficient due to enlargement of the Hilbert spaces and would require explicit relaxation terms if the nuclear spin states of the tryptophan were not simply randomized upon electron transfer.

![Diagram](image-url)

**FIG. 7.** Complex reaction scheme involving multiple spin systems. (a) The reaction scheme mainly consists of two spin systems, the $\lbrack \text{FAD}^\ast \cdots \cdot W^\ast_C \rbrack$ and $\lbrack \text{FAD}^\ast \cdots \cdot W^\ast_D \rbrack$ radical pairs inside a cryptochrome protein. The $\lbrack \text{FAD}^\ast \cdots \cdot W^\ast_C \rbrack$ radical pair is initially produced in a singlet spin state and may either recombine with rate constant $k_R$ from the singlet spin state to form the initial state or be transformed into the $\lbrack \text{FAD}^\ast \cdots \cdot W^\ast_D \rbrack$ radical pair with rate constant $k_{CD}$ by an electron transfer. The $\lbrack \text{FAD}^\ast \cdots \cdot W^\ast_D \rbrack$ radical pair may either react to form the spin-dependent singlet and triplet reaction products with rate constants $k_S$ and $k_T$, respectively, or transition back into the $\lbrack \text{FAD}^\ast \cdots \cdot W^\ast_C \rbrack$ radical pair with rate constant $k_{CD}$. (b) A simpler reaction scheme with only a single radical pair system which may also recombine with rate $k_R$ or produce distinct products from the singlet and triplet state with rate constants $k_S$ and $k_T$, respectively. (c) The time-evolution of an ensemble of spin systems following the reaction scheme in (a). (d) The time-evolution of an ensemble of spin systems following the reaction scheme in (b).
C. Complex time-dependences

Realistic spin systems often exhibit a large set of complex interactions which are not static but fluctuate over time due to, e.g., thermal motion in the protein hosting a radical pair. Rather than including such fluctuations of the Hamiltonian in spin chemical calculations, they are often described indirectly through relaxation terms such as provided by Redfield theory.\textsuperscript{48–50} Although the use of a relaxation operator can be useful in many situations, MolSpin allows us to define complex time-dependencies for any interaction or the rate “constants” of reaction operators. Thus, samples of thermal fluctuations in the interactions of a radical pair, for example, can be included directly in the spin dynamics calculations. Another example would be the exposure of a spin system to a radiofrequency radiation pulse;\textsuperscript{1} the pulse can be described by a complex time-dependence of an external magnetic field.

The complex time-dependences are described as time series for parameters such as the components of the hyperfine tensors or the components of an external magnetic field. There are no constraints on the time-resolution for the specified time series, and it does not have to be specified using a constant time step. MolSpin uses linear interpolation between the data points specified in the time series if needed. Complex time-dependences can, in principle, be used in all kinds of calculations in MolSpin; it is, for example, supported for time-evolution and quantum yield calculations, as well as for calculation of the time-evolution of the energy levels.

As an example, the spin dynamics in the [FAD$^*$...W$^*_C*] radical pair hosted by cryptochrome from Drosophila melanogaster was simulated, where the thermal motion of the protein was taken into account. A 200 ns long molecular dynamics (MD) trajectory of cryptochrome simulated earlier\textsuperscript{23} was used to obtain the thermal fluctuations in the orientation of the flavin moieties of the FAD$^*$ radical as well as the tryptophan W$^*_C$ radical. The trajectory from the MD simulation was repeated multiple times in order to simulate the spin dynamics for 5 μs, assuming a radical pair lifetime of 1 μs. Repeating the MD trajectory is justified as correlations in the local thermal fluctuations in the radicals are vanishing on a much shorter time scale than 200 ns. The isotropic part of the hyperfine coupling as well as the eigenvalues of the hyperfine tensor were assumed constant, such that only fluctuations in the orientation of the radicals, i.e., the orientation of the hyperfine tensors as well as the spin quantization axes, were included in the present calculation. The result of the calculation is illustrated in Fig. 8, where it is compared with a calculation using a static orientation of the radicals where a much larger magnetic field effect is seen. A smaller magnetic field effect was expected for the calculation with fluctuating orientations of the radicals as fluctuations typically act as a source of spin relaxation; these fluctuations in the orientations of the radicals correspond to a direct coupling to the thermal bath of the environment.

The spin dynamics calculation on cryptochrome including thermal fluctuations is only meant as a proof-of-concept calculation; making a proper calculation is more involved since (i) the spin dynamics must be simulated multiple times using different MD trajectory samples to obtain proper statistics, and (ii) hyperfine tensors should be calculated along the MD trajectories as not just their orientation but also their eigenvalues may change. Despite the difficulties involved in simulating realistic spin systems,\textsuperscript{9} MolSpin still has the ability to simulate even the most complex spin dynamics, and in fact, the name MolSpin—molecular spin dynamics—originates from a desire to perform realistic spin dynamics simulations by directly including the thermal fluctuations in interaction parameters that may be obtained from MD simulations.

H. Multiple interacting subsystems

All the examples above consider radical pair dynamics, but MolSpin is not restricted to calculations of such systems; it is also possible to study, for example, a radical pair interacting with a third scavenger radical,\textsuperscript{13,14} two radical pairs interacting with each other, radical-metal complex interactions, and much more. Another example is an Ising spin system where each spin interacts with its immediate neighbors on a lattice. The interaction between a pair of spins shares the same form of the interaction Hamiltonian,

\[
H_{ij} = \alpha S_i \cdot A \cdot S_j,
\]

where $\alpha$ and $A$ is a scalar and a tensor, respectively, describing the interaction between the two spins represented by their spin operators $S_i$ and $S_j$. $\alpha$ and $A$ are often constants but may also be time-dependent.

It was recently described how a scavenger radical may improve the sensitivity of a radical pair-based compass sensor,\textsuperscript{15} following a reaction scheme like the one illustrated in Fig. 9(a). Following the aforementioned work, the dynamical evolution of the three radicals is governed by an equation similar to Eq. (1),

\[
\frac{d\rho}{dt} = -i\hbar^{-1}[H, \rho] + \mathcal{V}(\rho) + \mathcal{R}(\rho),
\]

where $\mathcal{R}$ is a relaxation superoperator. The reaction superoperator is of the Haberkorn form,\textsuperscript{48–50}

\[
\mathcal{V}(\rho) = -\frac{k_8}{2} \langle P_{12S,\rho} \rangle - k_7 \rho - \frac{k_8}{2} \langle P_{23S,\rho} \rangle.
\]
The presence of a scavenger radical may alter radical pair dynamics. (a) The reaction scheme for a radical pair with a nearby scavenger radical, giving rise to three reaction pathways: the backreaction from the singlet state of the \([A^{\cdot\cdot}\cdots B^{\cdot\cdot}...C^{\cdot}]\) radical pair, a spin-independent forward reaction, and the scavenging reaction. It is assumed that the scavenging reaction only occurs from a singlet state between the \([B^{\cdot\cdot}\cdots C^{\cdot}]\) electronic spins. The superscript \(S\), \(D\), and \(Q\) refers to the singlet, doublet, and quartet spin states of the three radicals. (b) Model calculations with and without the presence of a scavenger, assuming \(A^{\cdot\cdot}\cdot\) to be \(FAD^{\bullet+}\) (including nuclei N5 and N10) and \(B^{\cdot\cdot}\) to be \(W^{\bullet}\) (including only nucleus N1); see the nuclei and coordinate frame in Fig. 3(c). The scavenger radical \(C^{\cdot}\) had no hyperfine interactions. The calculations assume \(k_1 = 0.1\,\mu s^{-1}\) and \(k_2 = 0.2\,\mu s^{-1}\).

where \(P_{1,2,5}\) is the radical pair singlet projection operator, while \(P_{23,5}\) is the projection operator onto the singlet state defined between one of the radicals of the pair and the scavenger radical; \(k_s\), \(k_f\), and \(k_r\) are the rate constants for electron backtransfer, the forward reaction, and the scavenging reaction, respectively. The relaxation superoperator has a Lindblad form,

\[
\mathcal{R}(\rho) = k_r \sum_{i} \left( S_{i\rho} - \frac{3}{4} S_{\rho} \right), \quad q \in \{x,y,z\}.
\]

Here, \(i\) refers to the three radicals and \(k_r\) is the spin relaxation rate. The initial state of the spin system is assumed to be a radical pair singlet. The quantum yield of the spin-independent forward reaction was calculated using MolSpin both with and without the presence of the scavenger radical, and the results are illustrated in Fig. 9(b).

The effect of the scavenger radical is illustrated in Fig. 9(b), which shows a significant change in the singlet quantum yield once the scavenger radical is present. The singlet yield for all magnetic field orientations \(\theta\) increases with the scavenging rate constant, \(k_s\), but the difference between the maximum and minimum singlet yields for different magnetic field orientations \(\theta\) reaches a maximum around 50 \(\mu s^{-1}\), consistent with the value of \(k_c = 51.8\,\mu s^{-1}\) which was recently reported to maximize the so-called singlet yield anisotropy in the present model radical pair.

It should be noted that this effect is caused exclusively by the spin-dependent nature of the scavenging reaction since no interaction between the scavenger and the radical pair was present; the scavenger radical only interacted with the geomagnetic field through the Zeeman interaction.

III. SOFTWARE ARCHITECTURE

Designing a program so general that all calculations involving spin dynamics can be performed is no trivial task, as such calculations can be both a series of known calculation types, such as those that are already implemented, but also any possible type of calculation that may be invented in the future. Since the requirements of future calculation types cannot be readily anticipated, the software architecture becomes important. Any spin dynamics calculation task will, however, always need certain elements: (i) a description of the spin system under consideration, (ii) special input parameters for the calculation method, (iii) freedom to define a custom output format, and (iv) an implementation of the calculation method itself. In order to accommodate these criteria, an object-oriented design strategy was adopted with the class hierarchy illustrated in Fig. 10. The class hierarchy consists of a variety of classes divided into three modules: the SpinAPI module describing spin systems, the MSDParser module handling the input files, and the RunSection module which runs the calculations and contains all the task classes. The SpinAPI module contains objects describing the physical system through a collection of SpinSystem objects, each with a collection of objects describing the system, and the information is stored such that access to the raw input data is available to task classes through a convenient interface. The SpinAPI module thus accommodates the first criteria, but since many calculation types rely on either the native Hilbert space or the Liouville space spanned by all the spins in the spin system or a subset of those, a helper class called SpinSpace provides easy access to matrix representations of Hamiltonians, state projection operators, and so on. The matrices are stored using the matrix classes provided by the Armadillo library, and the SpinSpace helper class is able to produce both dense and sparse matrices.

An important feature of MolSpin is the possibility to adapt the input file format to future needs, such as being able to specify additional parameters for calculation methods as mentioned in point (ii) above or to allow, e.g., Spin objects to have an additional properties such as mass or position. Parsing of the input files are handled by the MSDParser module, where the central class also carries the name MSDParser. The most important class when one needs to define new parameters in the input, however, is the ObjectParser. Whenever almost any object from the SpinAPI or RunSection modules is created, they are given an instance of ObjectParser. The ObjectParser instance contains all the information about an object that has been specified in the input file, for example, the spin quantum number in the Spin class or the field vector in the Interaction class, and...
all of these classes such as Spin and Interaction are instantiated by requesting the values associated with certain keywords from their ObjectParser instances. Adding a new parameter to an Interaction or Transition object could therefore be done simply by requesting an additional keyword from their ObjectParser instance. This is also true for task classes, so any new task class can request any number of special parameters from their ObjectParser instance.

Task classes have access to two output streams—a log stream and a data stream; both of these streams can be redirected to specific files. There is no restriction on the contents or formatting of data that can be written to those streams, so each task class can, in principle, determine how it wants to present its results. It may appear that a predefined output format would be more convenient, but since MolSpin is supposed to handle any kind of spin dynamics calculation, it would not be possible to determine a single format that would suit all possible future needs. It is, therefore, the responsibility of task class authors to provide a logical and coherent output format, and all the task classes implemented so far share a common format.

MolSpin has no limitation on the spin quantum numbers used, and all spin matrices are dynamically generated following the Flyweight design pattern, i.e., they are created only when requested and shared between all Spin objects with the same spin quantum number.

The BasicTask class provides a simple interface for derived classes to access all data about the spin systems, and the Armadillo library provides a simple interface to all the most common linear algebra operations such as vector and matrix arithmetic or eigenvalue decomposition, while relying on high-speed math libraries such as OpenBLAS or Intel MKL to carry out the computations. Implementing a new calculation algorithm in MolSpin is, therefore, at least as easy as in any other software tool or programming language.

A. Flexibility

In order to carry out complex computations, it is necessary to have fine-grained control of the various parameters specified for a spin system, such as the magnetic field orientation in Fig. 3(b) or the oscillation frequency in Fig. 4(a). MolSpin lets you define any number of Actions that allows you to change the various spin system parameters between calculation steps. Examples of these Actions could be a rotation or scaling of a vector such as the magnetic field vector or multiplying or adding a constant to a scalar such as a rate constant. Each Action has properties determining how often they should be performed, in case they should not be used after each computational step, and some Actions have special properties such as...
the rotation axis for the RotateVector Action. Almost any parameter in MolSpin can be modified by Actions, and the variety of Actions provides you with the fine-grained control and great flexibility in your calculations. Several examples of Actions can be found in the MolSpin input files in the supplementary material.

B. Extensibility

The key feature of MolSpin that allows it to be the most general spin dynamics software tool available is the huge emphasis on extensibility, allowing any calculation method invented in the future to be easily implemented. This feature is achieved by the use of a combination of Strategy and Template Method patterns. Adding a new task type to MolSpin is therefore a simple matter of creating a new class that inherits BasicTask.

Note also that MolSpin Actions, which are used to control how parameters change between calculation steps, are defined in a similar way using a Strategy pattern, such that the Action class plays a similar role to that of BasicTask with concrete actions being derived classes such as ActionAddScalar or ActionRotateVector. Similar to the way new task types can be created, new Action classes can, therefore, easily be created as well.

C. Parallelization

The heavy calculations are all delegated to the Armadillo library,\(^5\) which is a wrapper for a variety of high-speed math libraries, and most of these libraries, e.g., OpenBLAS\(^6\) or Intel MKL,\(^7\) use shared-memory parallelization. Shared-memory parallelization is, therefore, automatically supported through Armadillo.

MolSpin currently does not support distributed memory parallelization, i.e., MolSpin cannot utilize multiple nodes in a supercomputer cluster. Note, however, that many calculations are the so-called "embarrassingly parallel"; in particular, every calculation step is independent of the other calculation steps and can therefore be run in parallel. MolSpin has a series of options that makes it easy to run specific calculation steps, which makes it easy to distribute the workload between multiple compute nodes. See the supplementary material for an example of a script that distributes the work between multiple nodes.

IV. CONCLUSION

The MolSpin software tool provides powerful software architecture and a comprehensive and elaborate input file format that makes MolSpin a very powerful and universal tool: it is very easy to set up any kind of spin dynamics calculation. Still, very specialized calculation methods can also be implemented just as easily as general methods. The calculation methods that have been implemented so far are fairly basic and can perform all of the most common types of calculations on spin systems, except simulation of advanced EPR and NMR techniques, which is covered by other specialized software tools.

The scaling and benchmarking of MolSpin has been omitted in the discussion above despite efficiency being an important aspect of any simulation software package. This omission is mainly due to the versatility of MolSpin which makes it impossible to benchmark the software in any meaningful or useful way due to the amount of both specialized and general task classes, flexibility in defining the physical systems, as well as reliance upon external high-speed math libraries. One of the most general task classes can handle 5–6 spins due to the use of Liouville space, while the most effective but very specialized method currently can handle 16–20 spins within one or a few days, depending on the workstation. For the calculations presented in this paper, we used a workstation with a 2.60 GHz Intel Xeon E5-2697 v3 CPU and 224 GB RAM. Also note that task classes that involve time-dependent interactions are significantly more demanding than calculations with time-independent interactions.

It should also be noted that MolSpin is integrated in the VIKING platform,\(^7\) such that spin dynamics calculations can be carried out through a convenient interface which also offers tools for visualizing the results. Due to the general nature of MolSpin, only a subset of its features, focusing on radical pairs dynamics, is currently available through VIKING. For more complex calculations, MolSpin can be used as a standalone software.

The real strength of MolSpin lies not in its current calculation capabilities but in the great flexibility it offers and, in particular, in the extensibility that allows it to evolve; new and better calculation methods can easily be implemented and shared with collaborators, while retaining the flexibility and universality of MolSpin.

SUPPLEMENTARY MATERIAL

The supplementary material contains a brief introduction to the MolSpin input format and the input files for all of the calculation examples presented in the paper. The supplementary material additionally presents a script that illustrates how the workload of a MolSpin job can be distributed easily between multiple compute nodes on a supercomputer cluster.

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REFERENCES
