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ABSTRACT

In this paper, we outline a physically motivated framework for describing spin-selective recombination processes in chiral systems, from which we derive spin-selective reaction operators for recombination reactions of donor–bridge–acceptor molecules, where the electron transfer is mediated by chirality and spin–orbit coupling. In general, the recombination process is selective only for spin-coherence between singlet and triplet states, and it is not, in general, selective for spin polarization. We find that spin polarization selectivity only arises in hopping-mediated electron transfer. We describe how this effective spin-polarization selectivity is a consequence of spin-polarization generated transiently in the intermediate state. The recombination process also augments the coherent spin dynamics of the charge separated state, which is found to have a significant effect on the recombination dynamics and to destroy any long-lived spin polarization. Although we only consider a simple donor–bridge–acceptor system, the framework we present here can be straightforwardly extended to describe spin-selective recombination processes in more complex systems.

I. INTRODUCTION

There has recently been a growing interest in spin-selectivity of processes in molecular chiral donor–acceptor systems.[1–4] These systems may provide a versatile platform for exploring the molecular origins of the chirality-induced spin selectivity (CISS) effect,[5–8] without the complications of interactions with electrodes,[3,9–12] and it has also been suggested that chiral donor–acceptor systems could be exploited in various quantum information science applications.[1,13,14] Several theories have been proposed for the molecular CISS effect and on how spin polarization is generated in the formation of charge separated states,[7,8,15–17] and a handful of experimental protocols have been proposed to test these theories.[2,5,8,15,18] While most studies to date have focused on the CISS effect in the formation of charge separated states in donor–acceptor systems, it has also been suggested that CISS could play a role in the charge recombination of donor–acceptor systems.[8,15] However, the proposed theories of CISS in charge recombination are either limited to simple one-step electron transfer[15] or are purely phenomenological,[8] and thus far, the role of CISS in experimentally realized donor–bridge–acceptor systems[2,19–21] has not been explored. Motivated by this, in this paper, we aim to answer the question: Does chirality lead to spin-selective charge recombination in donor–bridge–acceptor molecules?

In systems where chirality and spin–orbit coupling have no effect on charge recombination of charge separated (CS) states, the treatment of spin-selective recombination is well understood.[22–25] We describe the system with a time-dependent spin density operator for the CS state, $\hat{\sigma}_{\mathrm{CS}}$, which spans the set of near-degenerate singlet and triplet spin states of the CS state. This spin density operator obeys the well-established Haberkorn quantum master equation

$$\frac{d}{dt}\hat{\sigma}_{\mathrm{CS}}(t) = -i[\hat{H}, \hat{\sigma}_{\mathrm{CS}}(t)] + \mathcal{K}\hat{\sigma}_{\mathrm{CS}}(t), \tag{1}$$

where $\hat{H}$ is the spin Hamiltonian for the CS state and $\mathcal{K}$ is the reaction superoperator, which is given by

$$\mathcal{K}\hat{\sigma}_{\mathrm{CS}} = -\{\hat{K}, \hat{\sigma}_{\mathrm{CS}}\} = -\left\{\frac{k_{\mathrm{CR,S}}}{2}\hat{P}_{\mathrm{S}} + \frac{k_{\mathrm{CR,T}}}{2}\hat{P}_{\mathrm{T}}, \hat{\sigma}_{\mathrm{CS}}\right\}, \tag{2}$$

in which and $k_{\mathrm{CR,S}}$ and $k_{\mathrm{CR,T}}$ are the singlet and triplet spin selective reaction rate constants, respectively, and $\hat{P}_{\mathrm{S}} = |\mathrm{S}\rangle\langle\mathrm{S}|$ and $\hat{P}_{\mathrm{T}} = \sum_{\alpha=x,y,z} |T_\alpha\rangle\langle T_\alpha|$ are projection operators onto singlet and triplet spin states of the CS state.[22,23,25] $\mathcal{K}$ describes the full effect of the reaction process on the dynamics of the CS state, and the reaction operator $\hat{K}$ encodes how population is lost from the CS state. In what follows, we will refer to $\mathcal{K}$ as the reaction *superoperator* and $\hat{K}$ as the reaction *operator*. It should be noted that this equation does not conserve the trace of $\hat{\sigma}_{\mathrm{CS}}$ because population is lost from the CS state by recombination, and it further assumes that the recombination of the CS state is irreversible.

It has been postulated by Luo and Hore that in chiral donor–acceptor systems, the reaction operator $\hat{K}$ for a CISS mediated recombination process should be given by[8]

$$\hat{K} = \frac{k_{\mathrm{CR}}}{2} |\phi_\chi\rangle\langle\phi_\chi|, \tag{3}$$

in which $|\phi_\chi\rangle = \cos(\chi/2)|\mathrm{S}\rangle + \sin(\chi/2)|\mathrm{T}_z\rangle$, $|\mathrm{S}\rangle = \frac{1}{\sqrt{2}}(|\uparrow_{\mathrm{D}}\downarrow_{\mathrm{A}}\rangle - |\downarrow_{\mathrm{D}}\uparrow_{\mathrm{A}}\rangle)$, and $|\mathrm{T}_z\rangle = \frac{1}{\sqrt{2}}(|\uparrow_{\mathrm{D}}\downarrow_{\mathrm{A}}\rangle + |\downarrow_{\mathrm{D}}\uparrow_{\mathrm{A}}\rangle)$, where the quantization axis, z, is the molecular frame spin-polarization axis, and the mixing angle χ is a phenomenological parameter that parameterizes the extent of spin polarization selectivity. This form of the reaction operator is based on the assumption that in a chiral molecule, the recombination process is partially spin selective, and it is straightforward to verify that the total decay rate of the CS state with this model is dependent on the difference in z-spin components on D and A, i.e., the spin-polarization $\langle \Delta S_z \rangle$ of the CS state (where the spin polarization operator is defined as $\Delta\hat{S}_z = \hat{S}_{\mathrm{D}z} - \hat{S}_{\mathrm{A}z}$). The limit of full spin-selectivity is recovered for $\chi = \pi/2$ and $|\phi_\chi\rangle = |\uparrow_{\mathrm{D}}\downarrow_{\mathrm{A}}\rangle$, where the recombination only occurs if the donor and acceptor electrons have specific opposite spin orientations in the molecular frame. It should be noted that this reaction operator has not been derived from any microscopic models of chirality induced spin selectivity, and there is no direct experimental evidence that it provides a reasonable model of spin selective recombination in chiral donor–acceptor systems.

In the previous work, we have derived a different reaction superoperator to that, given by Eq. (3), for a simple one-step electron transfer between a donor and an acceptor $\mathrm{D}^{\bullet+}$–$\mathrm{A}^{\bullet-} \to$ D–A, invoking the modest approximations.[25] Specifically, it is assumed that the coupling between the charge transfer states is weak, that the nuclear degrees of freedom are initially at local thermal equilibrium on one of the charge transfer potential energy surfaces, and that the Condon approximation holds for the direct charge transfer coupled, V_{DA}, and the spin–orbit mediated charge transfer coupling Λ_{DA} (essentially the same approximations as Marcus theory[26–28]). The model electronic Hamiltonian for the singlet and triplet $\mathrm{D}^{\bullet+}$–$\mathrm{A}^{\bullet-}$ (CS) and D–A (S_0) states in this theory is given by

$$\begin{aligned}\hat{H}_{\mathrm{DA}} = E_{\mathrm{S}_0}|\mathrm{S}_0\rangle\langle\mathrm{S}_0| &+ \sum_{\Theta=\mathrm{S},\mathrm{T}_x,\mathrm{T}_y,\mathrm{T}_z} E_{\mathrm{CS},\Theta}|\mathrm{CS},\Theta\rangle\langle\mathrm{CS},\Theta| \\ &+ V_{\mathrm{DA}}(|\mathrm{CS},\mathrm{S}\rangle\langle\mathrm{S}_0| + |\mathrm{S}_0\rangle\langle\mathrm{CS},\mathrm{S}|) \\ &+ i\frac{\Lambda_{\mathrm{DA}}}{2}(|\mathrm{CS},\mathrm{T}_z\rangle\langle\mathrm{S}_0| - |\mathrm{S}_0\rangle\langle\mathrm{CS},\mathrm{T}_z|),\end{aligned} \tag{4}$$

and from this, the reaction superoperator can be derived to be

$$\mathcal{K}\hat{\sigma}_{\mathrm{CS}} = -\left\{\frac{k_{\mathrm{CR}}}{2}|\psi_\theta\rangle\langle\psi_\theta|, \hat{\sigma}_{\mathrm{CS}}\right\} - i[\delta\epsilon|\psi_\theta\rangle\langle\psi_\theta|, \hat{\sigma}_{\mathrm{CS}}], \tag{5}$$

where $|\psi_\theta\rangle = \cos\theta|\mathrm{S}\rangle + i\sin\theta|\mathrm{T}_z\rangle$, with $\tan\theta = \Lambda_{\mathrm{DA}}/(2V_{\mathrm{DA}})$, where the quantization axis z is defined by the molecular frame spin–orbit coupling vector. This state is not spin polarized, i.e., $\langle S_{\mathrm{D}z}\rangle = \langle S_{\mathrm{A}z}\rangle = \langle \Delta S_z\rangle = 0$, so, in this case, the recombination process is not selective for spin polarization. However, the recombination process is selective for the imaginary part of the coherence between $|\mathrm{S}\rangle$ and $|\mathrm{T}_z\rangle$ states, measured by the operator $\hat{\Pi}_{\mathrm{ST}_z} = -i(|\mathrm{S}\rangle\langle\mathrm{T}_z| - |\mathrm{T}_z\rangle\langle\mathrm{S}|)/2$, which we refer to simply as the $\mathrm{S}-\mathrm{T}_z$ coherence. The shift term $\delta\epsilon \approx (V_{\mathrm{DA}}^2 + (\Lambda_{\mathrm{DA}}/2)^2)/(E_{\mathrm{S}_0} - E_{\mathrm{CS}})$ appearing in this reaction superoperator is a superexchange mediated spin–orbit coupling interaction in the CS state that emerges as a result of the spin–orbit interaction between the CS state and the S_0 ground-state, which cannot, in general, be neglected.[7,15]

In the subsequent work, it was found that an interplay of spin–orbit coupling and exchange interactions in a two-step charge separation following photo-excitation can produce spin polarization, whereas a single-step electron transfer cannot.[7] This naturally raises the question: What role does chirality-induced spin selectivity play in the charge *recombination* of a donor–bridge–acceptor system? To address this question, we will consider charge recombination in a chiral D–B–A molecule and derive a reaction operator that describes the superexchange and incoherent hopping limits of the charge recombination process.

II. CISS IN DONOR–BRIDGE–ACCEPTOR CHARGE RECOMBINATION

As a minimal model for a spin–orbit coupling mediated charge recombination process in a chiral donor–acceptor system, we consider the recombination of a donor–bridge–acceptor system from a charge separated (CS) state, $\mathrm{D}^{\bullet+}$–B–$\mathrm{A}^{\bullet-}$, back to a closed shell ground state (S_0), D–B–A. We will also assume that direct $\mathrm{A}^{\bullet-} \to \mathrm{D}^{\bullet+}$ tunneling of the electron does not occur, so, the electron either hops via an intermediate $\mathrm{CS}^\star$ state, $\mathrm{D}^{\bullet+}$–$\mathrm{B}^{\bullet-}$–A, in which the bridge B is charged, or the electron tunnels via indirect superexchange coupling through virtual transitions to intermediate charge transfer states. Both the CS and $\mathrm{CS}^\star$ states can exist in either singlet or triplet electron spin states, whereas the S_0 ground state is assumed to exist only in a pure singlet state. For simplicity we will assume that only the $\mathrm{B}^{\bullet-} \to \mathrm{D}^{\bullet+}$ electron transfer is mediated by spin–orbit coupling, and that the initial hopping step is not spin selective. The transition from superexchange mediated tunneling to hopping is controlled by the energy of the $\mathrm{CS}^\star$ state (at fixed electron transfer reorganization energy). When the intermediate $\mathrm{CS}^\star$ state is very high in energy (compared to thermal energy $k_{\mathrm{B}}T$), hopping is unfeasible; thus, superexchange dominates, but when the intermediate $\mathrm{CS}^\star$ is thermally accessible, hopping becomes the dominant mechanism.[26,29,30] This is illustrated schematically in Fig. 1.[20,29] For simplicity, we ignore any direct tunneling between D and A, which is justified, given that direct tunneling would require overlap between D and A orbitals, which would be minimal in this system due to the spatial separation of D and A by B.

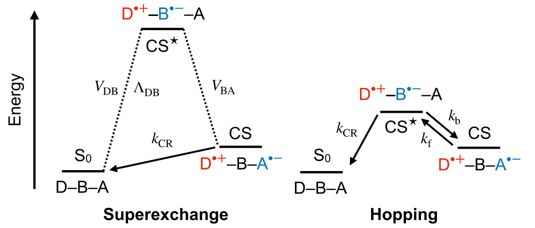

FIG. 1. Diagram summarizing the charge transfer states involved in the donor–bridge–acceptor system, indicating the incoherent rate processes with arrows and superexchange coupling with dashed lines, for the superexchange limit (left) and hopping limit (right).

Within this model, the spin quantization (i.e., the spin polarization axis) is defined by the spin–orbit coupling vector between the $D^{\bullet+}$–$B^{\bullet-}$–A and $D^{\bullet+}$–B–$A^{\bullet-}$ states. Assuming an effective one-electron picture, this vector is given by $i\boldsymbol{\Lambda}_{\mathrm{DB}} = \sum_\alpha \int d\mathbf{r}\, \psi_{\mathrm{D}}(\mathbf{r}) \hat{\xi}_\alpha \hat{\boldsymbol{\ell}}_\alpha \psi_{\mathrm{B}}(\mathbf{r})$, where the sum is over nuclei in the molecule, $\psi_{\mathrm{D}}(\mathbf{r})$ is the donor localized electron orbital wavefunction, $\psi_{\mathrm{D}}(\mathbf{r})$ is the bridge localized orbital wave-function, $\hat{\xi}_\alpha$ is a function of the electron distance from nucleus α, and $\hat{\boldsymbol{\ell}}_\alpha$ is the orbital angular momentum about the nucleus α. This vector $\boldsymbol{\Lambda}_{\mathrm{DB}}$, defining the quantization axis, can be computed using *ab initio* methods or its direction can be approximated with simple symmetry-based physical arguments. For example, for electron transport between covalently linked π-systems, as in Ref. 19, this vector lies approximately along the direction of charge transfer. This follows from the fact that for two orthogonal p-orbitals on covalently linked atoms, this vector lies along the axis linking the atoms, which would approximately coincide with the charge transfer axis.[31] (Further discussion of the SOC vector can be found in the supplementary material of Ref. 15 and the references therein.)

A. The superexchange limit

First, in order to understand the superexchange mediated electron transfer limit, we consider the following model for the electronic Hamiltonian for the S_0, CS, and CS* states:[7,26,29]

$$\begin{aligned}\hat{H}_{\mathrm{DBA}} = {} & E_{\mathrm{S}_0}|\mathrm{S}_0\rangle\langle \mathrm{S}_0| + \sum_{\Theta=\mathrm{S},\mathrm{T}_x,\mathrm{T}_y,\mathrm{T}_z} E_{\mathrm{CS}^\star,\Theta}|\mathrm{CS}^\star,\Theta\rangle\langle \mathrm{CS}^\star,\Theta| \\ & + \sum_{\Theta=\mathrm{S},\mathrm{T}_x,\mathrm{T}_y,\mathrm{T}_z} E_{\mathrm{CS},\Theta}|\mathrm{CS},\Theta\rangle\langle \mathrm{CS},\Theta| \\ & + \sum_{\Theta=\mathrm{S},\mathrm{T}_x,\mathrm{T}_y,\mathrm{T}_z} V_{\mathrm{BA}}\big(|\mathrm{CS}^\star,\Theta\rangle\langle \mathrm{CS},\Theta| + |\mathrm{CS},\Theta\rangle\langle \mathrm{CS}^\star,\Theta|\big) \\ & + V_{\mathrm{DB}}\big(|\mathrm{CS}^\star,\mathrm{S}\rangle\langle \mathrm{S}_0| + |\mathrm{S}_0\rangle\langle \mathrm{CS}^\star,\mathrm{S}|\big) \\ & + \frac{i\Lambda_{\mathrm{DB}}}{2}\big(|\mathrm{CS}^\star,\mathrm{T}_z\rangle\langle \mathrm{S}_0| - |\mathrm{S}_0\rangle\langle \mathrm{CS}^\star,\mathrm{T}_z|\big). \qquad (6)\end{aligned}$$

Here, $\Theta = \mathrm{S}$, T_x, T_y or T_z, denotes the total electron spin state for the charge separated states, V_{DB} and V_{BA} denote the spin-conserving diabatic (i.e., direct tunneling) couplings between electronic states, and Λ_{DB} denotes the spin–orbit coupling between the CS* and S_0 ground state. For simplicity, we assume that SOC only mediates the D ↔ B coupling, but the general result that we obtain holds when SOC mediates the B ↔ A electron transfer process as well. We also assume that direct and spin–orbit mediated D ↔ A couplings are negligible due to the spatial separation of D and A.

In the superexchange mediated electron transfer limit, where $E_{\mathrm{CS}^\star,\Theta} \gg E_{\mathrm{CS},\Theta}, E_{\mathrm{S}_0}$, we do not need to explicitly include the intermediate charged bridge state, CS*, and we can treat the charge recombination of the CS state to the S_0 state as a two-electron-transfer-state problem, with an effective Hamiltonian given by

$$\begin{aligned}\hat{H}_{\mathrm{DBA,eff}} = {} & (E_{\mathrm{S}_0} + \delta E_{\mathrm{S}_0})|\mathrm{S}_0\rangle\langle \mathrm{S}_0| \\ & + \sum_{\Theta=\mathrm{S},\mathrm{T}_x,\mathrm{T}_y,\mathrm{T}_z} (E_{\mathrm{CS},\Theta} + \delta E_{\mathrm{CS},\Theta})|\mathrm{CS},\Theta\rangle\langle \mathrm{CS},\Theta| \\ & + V_{\mathrm{DA,eff}}(|\mathrm{CS},\mathrm{S}\rangle\langle \mathrm{S}_0| + |\mathrm{S}_0\rangle\langle \mathrm{CS},\mathrm{S}|) \\ & + i\frac{\Lambda_{\mathrm{DA,eff}}}{2}(|\mathrm{CS},\mathrm{T}_z\rangle\langle \mathrm{S}_0| - |\mathrm{S}_0\rangle\langle \mathrm{CS},\mathrm{T}_z|). \qquad (7)\end{aligned}$$

A derivation of this effective Hamiltonian is given in Appendix A. We see from this that in the superexchange limit, there is an effective spin-conserving diabatic coupling between the S_0 and CS states, given by $V_{\mathrm{DA,eff}} = V_{\mathrm{DB}} V_{\mathrm{BA}}/(\bar{E} - E_{\mathrm{CS}^\star,\mathrm{S}})$, as well as an effective spin–orbit interaction, with coupling strength $\Lambda_{\mathrm{DA,eff}} = \Lambda_{\mathrm{DB}} V_{\mathrm{BA}}/(\bar{E} - E_{\mathrm{CS}^\star,\mathrm{T}_z})$, where $\bar{E}$ is the average energy of the S_0 and CS states.

Because the electronic Hamiltonian reduces to an effective two-state model in the superexchange limit, the electron transfer can be regarded as occurring in a single step

$$\mathrm{D}^{\bullet+} - \mathrm{B} - \mathrm{A}^{\bullet-} \xrightarrow{k_{\mathrm{CR}}} \mathrm{D{-}B{-}A}.$$

The electron transfer rate k_{CR} is mediated by the spin-conserving superexchange coupling term $V_{\mathrm{DA,eff}}$, and the spin–orbit coupling mediated superexchange coupling $\Lambda_{\mathrm{DA,eff}}$, and (when the Condon approximation is applied to the interstate superexchange couplings[26]) the theory reduces to that presented in Ref. 15, and the recombination superoperator is given exactly by Eq. (5), where $\Lambda_{\mathrm{DA}} = \Lambda_{\mathrm{DA,eff}}$ and $V_{\mathrm{DA}} = V_{\mathrm{DA,eff}}$. We see that in the superexchange limit, there is no selectivity for spin-polarization and only selectivity for spin-coherence.

B. The hopping limit

In the limit where charge recombination is controlled by hopping via an intermediate charge-separated state in which the bridge is charged,[29] $D^{\bullet+}$–$B^{\bullet-}$–A, which we denote CS*, the kinetic scheme for this mechanism is simply

$$\mathrm{D}^{\bullet+} - \mathrm{B} - \mathrm{A}^{\bullet-} \underset{k_{\mathrm{b}}}{\overset{k_{\mathrm{f}}}{\rightleftharpoons}} \mathrm{D}^{\bullet+} - \mathrm{B}^{\bullet-} - \mathrm{A} \xrightarrow{k_{\mathrm{CR}}} \mathrm{D} - \mathrm{B} - \mathrm{A}.$$

The forward and backward hopping rates are given by k_{f} and k_{b}, respectively, and the recombination from the CS* state is assumed to occur irreversibly at a rate k_{CR}. We start by writing down coupled equations of motion for the spin density operators of the CS* [$D^{\bullet+}$–$B^{\bullet-}$–A] and CS [$D^{\bullet+}$–B–$A^{\bullet-}$] states, as derived in Refs. 7, 15, and 25,

$$\begin{aligned}\frac{d}{dt}\hat{\sigma}_{\mathrm{CS}^\star}(t) = {} & -\Big\{\frac{k_{\mathrm{CR}}}{2}|\psi_\theta\rangle\langle\psi_\theta|, \hat{\sigma}_{\mathrm{CS}^\star}(t)\Big\} - k_{\mathrm{b}}\hat{\sigma}_{\mathrm{CS}^\star}(t) \\ & - i[\delta\epsilon|\psi_\theta\rangle\langle\psi_\theta| + 2J\hat{P}_{\mathrm{S}}, \hat{\sigma}_{\mathrm{CS}^\star}(t)] + k_{\mathrm{f}}\hat{\sigma}_{\mathrm{CS}}(t) \\ = {} & \mathcal{L}_{\mathrm{CS}^\star}\hat{\sigma}_{\mathrm{CS}^\star}(t) + k_{\mathrm{f}}\hat{\sigma}_{\mathrm{CS}^\star}(t), \qquad (8)\end{aligned}$$

$$\frac{d}{dt}\hat{\sigma}_{\mathrm{CS}}(t) = -i[\hat{H}, \hat{\sigma}_{\mathrm{CS}}(t)] + k_{\mathrm{b}}\hat{\sigma}_{\mathrm{CS}^\star}(t) - k_{\mathrm{f}}\hat{\sigma}_{\mathrm{CS}}(t), \tag{9}$$

where $\mathcal{L}_{\mathrm{CS}^\star} = -\{k_{\mathrm{CR}}/2|\psi_\theta\rangle\langle\psi_\theta|, \cdot\} - k_{\mathrm{b}} - i[\delta\epsilon|\psi_\theta\rangle\langle\psi_\theta| + 2\ J\hat{P}_{\mathrm{S}}, \cdot]$. Here, we have assumed that the intermediate state is sufficiently short-lived that we need only include the exchange interaction J and the spin–orbit coupling shift term $\delta\epsilon$ in the spin Hamiltonian for the $\mathrm{CS}^\star$ state, and we can safely neglect hyperfine, dipolar, and Zeeman interaction terms. This equation assumes that there is no long-lived coherence between different charge transfer states, and, thus, individual hopping steps can be treated as incoherent processes. We also assume that the $\mathrm{CS}^\star$ spin states are near-degenerate (relative to thermal energy), so, we do not need to account for spin-selectivity in the forward/backward hopping processes.[7]

Before proceeding further, we will outline a qualitatively how spin polarization selectivity can emerge in hopping-mediated charge recombination. When spin–orbit coupling mediates the charge recombination from the intermediate $\mathrm{CS}^\star$ state, it will selectively remove the $|\psi_\theta\rangle$ state. Molecules in electron spin states orthogonal to $|\psi_\theta\rangle$, which have a non-zero spin-coherence, e.g., $|\psi_{\theta\perp}\rangle = \sin\theta|\mathrm{S}\rangle - i\cos\theta|\mathrm{T}_z\rangle$, will not react, and, subsequently, they will evolve coherently under the exchange interaction J in the intermediate state to generate a spin- polarized state.[7]

This spin polarization is then transferred back to the CS state. In this sense, we see that the effective loss of spin polarization from the CS state is a result of the opposite spin polarization being generated in the intermediate state in molecules that do not recombine, which is transferred back to the CS state.

In order to derive the effective reaction superoperator, we apply the steady-state approximation (SSA) to the $\mathrm{CS}^\star$ spin density operator, $\frac{d}{dt}\hat{\sigma}_{\mathrm{CS}^\star}(t) \approx 0$, from which we obtain the following equation for the $\mathrm{CS}^\star$ density operator in terms of the CS density operator:

$$\hat{\sigma}_{\mathrm{CS}^\star}(t) \approx -k_{\mathrm{f}}\mathcal{L}^{-1}_{\mathrm{CS}^\star}\hat{\sigma}_{\mathrm{CS}}(t), \tag{10}$$

and from this, we can obtain the effective reaction superoperator as

$$\mathcal{K}\hat{\sigma}_{\mathrm{CS}}(t) = -k_{\mathrm{f}}(1 + k_{\mathrm{b}}\mathcal{L}^{-1}_{\mathrm{CS}^\star})\hat{\sigma}_{\mathrm{CS}}(t). \tag{11}$$

Alternatively, we can derive the hopping reaction superoperator without invoking the steady state approximation by first solving Eq. (8) for $\hat{\sigma}_{\mathrm{CS}^\star}(t)$ to give

$$\hat{\sigma}_{\mathrm{CS}^\star}(t) = k_{\mathrm{f}}\int_0^t d\tau\, e^{\mathcal{L}_{\mathrm{CS}^\star}\tau}\hat{\sigma}_{\mathrm{CS}}(t-\tau). \tag{12}$$

Assuming that $e^{\mathcal{L}_{\mathrm{CS}^\star}\tau}$ decays to zero on a time-scale faster than the dynamics of $\hat{\sigma}_{\mathrm{CS}}(t-\tau)$, we can invoke a Markovian approximation, where we replace $\hat{\sigma}_{\mathrm{CS}}(t-\tau) \to \hat{\sigma}_{\mathrm{CS}}(t)$ in the integral, and we set the upper limit of the integral to $\tau = \infty$. With this, we arrive at the same result as the steady-state approximation for $\hat{\sigma}_{\mathrm{CS}^\star}(t)$, given by Eq. (10), but this approach shows that the SSA approximation can be expected to be accurate, provided that the spin dynamics of the $\mathrm{CS}^\star$ occur on a much faster time scale than those of the CS state. Unfortunately, this reaction superoperator does not reduce to a simple form in the general case, although an analytical expression can be obtained. However, we can examine particular limits and extract the effective reaction operator $\hat{K}$.

First, it is instructive to consider the case where $\theta = 0$ and $\delta\epsilon = 0$, i.e., when there is no spin–orbit coupling involved in the charge recombination process and there is no CISS effect. In this case, the reaction operator reduces to

$$\mathcal{K}\hat{\sigma}_{\mathrm{CS}} = -\left\{\frac{\tilde{k}_{\mathrm{CR}}}{2}\hat{P}_{\mathrm{S}}, \hat{\sigma}_{\mathrm{CS}}\right\} - i\left[2\tilde{J}\hat{P}_{\mathrm{S}}, \hat{\sigma}_{\mathrm{CS}}\right] + \tilde{k}_{\mathrm{D}}\left(\hat{P}_{\mathrm{S}}\hat{\sigma}_{\mathrm{CS}}\hat{P}_{\mathrm{S}} - \frac{1}{2}\left\{\hat{P}_{\mathrm{S}}, \hat{\sigma}_{\mathrm{CS}}\right\}\right), \tag{13}$$

where $\tilde{k}_{\mathrm{CR}} = k_{\mathrm{f}}k_{\mathrm{b}}/(k_{\mathrm{b}} + k_{\mathrm{CR}})$ is the effective reaction rate, $2\tilde{J} = 8\ Jk_{\mathrm{b}}k_{\mathrm{f}}/[(4\ J)^2 + (k_{\mathrm{CR}} + 2k_{\mathrm{b}})^2]$ is an effective exchange coupling, and $\tilde{k}_{\mathrm{D}} = k_{\mathrm{f}}((4\ J)^2 + k_{\mathrm{CR}}(k_{\mathrm{CR}} + 2k_{\mathrm{b}}))/[(4\ J)^2 + (k_{\mathrm{CR}} + 2k_{\mathrm{b}})^2] - \tilde{k}_{\mathrm{CR}}/2$, is an effective singlet–triplet dephasing rate. In the limit where $J = 0$, we can similarly obtain a simple expression for the reaction operator

$$\begin{aligned}\mathcal{K}\hat{\sigma}_{\mathrm{CS}} = &-\left\{\frac{\tilde{k}_{\mathrm{CR}}}{2}|\psi_\theta\rangle\langle\psi_\theta|, \hat{\sigma}_{\mathrm{CS}}\right\} - i[\delta\tilde{\epsilon}|\psi_\theta\rangle\langle\psi_\theta|, \hat{\sigma}_{\mathrm{CS}}]\\ &+ \tilde{k}_{\mathrm{D}}\left(|\psi_\theta\rangle\langle\psi_\theta|\hat{\sigma}_{\mathrm{CS}}|\psi_\theta\rangle\langle\psi_\theta| - \frac{1}{2}\{|\psi_\theta\rangle\langle\psi_\theta|, \hat{\sigma}_{\mathrm{CS}}\}\right),\end{aligned} \tag{14}$$

where the effective charge recombination rate $\tilde{k}_{\mathrm{CR}}$, decoherence rate $\tilde{k}_{\mathrm{D}}$, and spin–orbit interaction $\delta\tilde{\epsilon}$ are given by the above expressions with the simple replacement $2J \to \delta\epsilon$. In each case, we see that the effective recombination operator can be decomposed into a shift in the spin Hamiltonian $\delta\hat{H}$, a Lindbladian decoherence term, with Lindblad rates, and operators $\gamma_{j,}$ and $\hat{L}_j$, and a reaction term with the reaction operator $\hat{K}$,

$$\begin{aligned}\mathcal{K}\hat{\sigma}_{\mathrm{CS}} = &-\left\{\hat{K}, \hat{\sigma}_{\mathrm{CS}}\right\} - i\left[\delta\hat{H}, \hat{\sigma}_{\mathrm{CS}}\right]\\ &+ \sum_j \gamma_j\left(\hat{L}_j\hat{\sigma}_{\mathrm{CS}}\hat{L}^\dagger_j - \frac{1}{2}\left\{\hat{L}^\dagger_j\hat{L}_j, \hat{\sigma}_{\mathrm{CS}}\right\}\right).\end{aligned} \tag{15}$$

First, we will consider the reaction operator $\hat{K}$, although the decoherence and Hamiltonian shift terms cannot, in general, be neglected, and we will later evaluate their importance. In general, $\hat{K}$ can be decomposed into the following set of operators:

$$\hat{K} = \frac{\tilde{k}_{\mathrm{S}}}{2}\hat{P}_{\mathrm{S}} + \frac{\tilde{k}_{\mathrm{T}_z}}{2}\hat{P}_{\mathrm{T}_z} + \frac{\tilde{k}_z}{2}\Delta\hat{S}_z + \frac{\tilde{k}_{\mathrm{ST}_z}}{2}\hat{\Pi}_{\mathrm{ST}_z}, \tag{16}$$

where $\hat{P}_{\mathrm{T}_z} = |\mathrm{T}_z\rangle\langle\mathrm{T}_z|$ is a projection operator onto the T_z state, $\Delta\hat{S}_z = (|\mathrm{S}\rangle\langle\mathrm{T}_z| + |\mathrm{T}_z\rangle\langle\mathrm{S}|)/2 = |{\uparrow_{\mathrm{D}}}{\downarrow_{\mathrm{A}}}\rangle\langle{\uparrow_{\mathrm{D}}}{\downarrow_{\mathrm{A}}}| - |{\downarrow_{\mathrm{D}}}{\uparrow_{\mathrm{A}}}\rangle\langle{\downarrow_{\mathrm{D}}}{\uparrow_{\mathrm{A}}}|$ is the spin polarization operator, and $\hat{\Pi}_{\mathrm{ST}_z} = -i(|\mathrm{S}\rangle\langle\mathrm{T}_z| - |\mathrm{T}_z\rangle\langle\mathrm{S}|)/2$ is the spin coherence operator. In general, the rates must satisfy $\tilde{k}_{\mathrm{S}}, \tilde{k}_{\mathrm{T}_z} \geq 0$ and $\tilde{k}_{\mathrm{S}}\tilde{k}_{\mathrm{T}_z} \geq (\tilde{k}^2_{\mathrm{ST}_z} + \tilde{k}^2_z)/4$ in order to preserve positivity of the density operator. We note that in the case of Luo and Hore's phenomenological theory, we have $\tilde{k}_{\mathrm{S}} = k_{\mathrm{CR}}\cos^2(\chi/2)$, $\tilde{k}_{\mathrm{T}_z} = k_{\mathrm{CR}}\sin^2(\chi/2)$, $\tilde{k}_z = k_{\mathrm{CR}}\ \sin(\chi)$, and $\tilde{k}_{\mathrm{ST}_z} = 0$.[8]

We find, in general, that both $\tilde{k}_z$ and $\tilde{k}_{\mathrm{ST}_z}$ are proportional to $\sin(2\theta)$, meaning that they only emerge in chiral systems. This is because the spin coherence that is generated by the spin–orbit mediated recombination is proportional to $\sin(2\theta)$. Furthermore, we find that the ratio of $\tilde{k}_z$ to $\tilde{k}_{\mathrm{ST}_z}$ is given by

$$\frac{\tilde{k}_z}{\tilde{k}_{\mathrm{ST}_z}} = \frac{4J(2k_{\mathrm{b}} + k_{\mathrm{CR}})}{(2k_{\mathrm{b}} + k_{\mathrm{CR}})^2 + 4\delta\epsilon^2 + 8J\delta\epsilon\ \cos 2\theta}, \tag{17}$$

which shows that spin polarization selectivity can only arise if J is non-zero, and if the back reaction and charge recombination from the intermediate state are sufficiently slow to allow some degree of coherent spin evolution in the intermediate state to generate spin polarization.

The full expressions for the spin-selective rate constants are somewhat cumbersome, although straightforward to evaluate numerically, so, here, we will analyze some of their properties in specific limits. In Appendix B, we show how to obtain $\mathcal{K}$ in the weak spin–orbit coupling limit, which we expect to be applicable to many organic donor–bridge–acceptor systems where the reaction superoperator parameters are relatively simple. In this limit, we find there are two dominant decoherence processes, with Lindblad operators $\hat{L}_j = \hat{P}_S$ and $\hat{P}_{T_z}$, and the recombination process is selective for both the S and T_z states, as well as for the spin polarization and S-T_z coherence $\hat{\Pi}_{ST_z}$. We also find that the spin-coherence and the spin-polarization selectivity only emerge at first-order in the spin orbit coupling, and spin-polarization selectivity is only non-zero if J is non-zero.

Starting from the weak spin–orbit coupling limit results in Appendix B, it is instructive to consider the limit where coherent dynamics of the CS* spins are much slower than the incoherent recombination process, i.e., $k_b, k_{CR} \gg J, \delta\epsilon$. In this limit, we find

$$\tilde{k}_S \approx \cos^2\theta \frac{k_f k_{CR}}{k_{CR}+k_b}, \quad \tilde{k}_{T_z} \approx \sin^2\theta \frac{k_f k_{CR}}{k_b}, \tag{18a}$$

$$\tilde{k}_{ST_z} \approx \sin(2\theta)\frac{k_f k_{CR}}{k_{CR}+k_b}, \quad \tilde{k}_z \approx \frac{k_f k_{CR}}{k_{CR}+k_b}\frac{4J\sin 2\theta}{2k_b+k_{CR}}. \tag{18b}$$

We see that the spin polarization that is removed from the CS state is proportional to J in the intermediate state. Conversely, in the limit where $J \gg k_b, k_{CR}, \delta\epsilon$, it can be found that $\tilde{k}_z \approx 0$ and $\tilde{k}_{ST_z} \approx 0$. This is because, in the large J limit, the spin polarization generated by the exchange interaction oscillates many times in the intermediate state prior to transfer back to the CS state, which averages the spin polarization that is transferred back to zero.

It is also interesting to consider the limit where k_{CR} is small and $\delta\epsilon = 0$. In this case, we find

$$\tilde{k}_S \approx \cos^2\theta \frac{k_f k_{CR}}{k_b}, \quad \tilde{k}_{T_z} \approx \sin^2\theta \frac{k_f k_{CR}}{k_b}, \tag{19a}$$

$$\tilde{k}_{ST_z} \approx \frac{k_f k_{CR} k_b \sin 2\theta}{k_b^2+(2J)^2}, \quad \tilde{k}_z \approx \frac{(2J) k_f k_{CR} \sin 2\theta}{k_b^2+(2J)^2}. \tag{19b}$$

In this case, if the initial charge separation goes via the same intermediate CS* state and if the initial charge separation following photo-excitation forms the CS* state in the $|\psi_\theta\rangle$ state, i.e., assuming $\Lambda_{D^\star B}/V_{D^\star B} = \Lambda_{DB}/V_{DB}$ (where D* denotes the excited precursor donor orbital), the spin polarization in the initial CS state is $-(2\,J)k_b \sin 2\theta/(k_b^2 + (2\,J)^2)$, and the initial spin coherence is $k_b^2 \sin 2\theta/(k_b^2 + (2\,J)^2)$. So, in this limit, the charge recombination is selective for the same spin-coherence as is initially generated, but with the *opposite* spin polarization. It is straightforward to show that this result also holds in the case where $\delta\epsilon \neq 0$. It should be noted that the situation is more complicated if the phase $\Lambda_{D^\star B}/V_{D^\star B}$ is different from Λ_{DB}/V_{DB}, which could be the case in a real system.

We now turn to the shift term, $\delta\hat{H}$, in the full effective reaction superoperator, which arises from the coherent dynamics that occur transiently in the intermediate state. We can expand this shift term in terms of the operators $\hat{P}_S$, $\hat{P}_{T_z}$, $\Delta\hat{S}_z$, and $\hat{\Pi}_{ST_z}$, as was done for $\hat{K}$:

$$\delta\hat{H} = \delta\tilde{\epsilon}_S\hat{P}_S + \delta\tilde{\epsilon}_{T_z}\hat{P}_{T_z} + \delta\tilde{\epsilon}_z\Delta\hat{S}_z + \delta\tilde{\epsilon}_{ST_z}\hat{\Pi}_{ST_z}. \tag{20}$$

Evaluating the reaction superoperator, we find, in general, that $\delta\tilde{\epsilon}_z = 0$, while the other terms are non-zero. The non-zero terms account for the shift in energy of the singlet and triplet states due to the exchange coupling in the intermediate state, and an effective spin–orbit coupling that arises due to the superexchange spin–orbit interaction in the CS* state [the term proportional to $\delta\epsilon$ in Eq. (8)]. As with $\hat{K}$, it is possible to obtain an exact expression for $\delta\hat{H}$, but it is very complicated; however in the weak spin–orbit coupling limit (presented in Appendix B), it is relatively straightforward to evaluate. The presence of this shift term (and the decoherence terms) couples and subsequently mixes the Remove space after hyphen. states of the CS state, which means that there exists no "protected" spin polarized CS state that can be generated from a non-polarized initial spin state. Importantly, this implies that there can be no long-lived spin polarization in the CS state. In the numerical tests presented in Sec. III, we will show that this shift term is essential in accurately calculating the spin polarization and coherence dynamics of the CS state.

In this analysis, we have only considered a simple model where there is a single intermediate charge transfer state and a single SOC mediated electron transfer step. However, the framework that we have employed here can be extended straightforwardly to include multiple intermediate states and multiple SOC-mediated electron transfer steps. In these more complex cases, analytic results are likely not tractable, although the functional form of the reaction operator and the shift term would be the same, and the framework used here can still be applied to compute the full effective reaction superoperator numerically.

III. NUMERICAL TESTS FOR THE HOPPING LIMIT

In this section, we aim to evaluate the accuracy of the steady state approximation used in Sec. II B to obtain the reaction superoperator, as well as the relative importance of spin selectivity in the reaction operator $\hat{K}$ and the augmented spin dynamics generated by $\delta\hat{H}$. As a first test, in Fig. 2, we show the dynamics of the CS state population and the spin polarization in the CS state as a function of time for the CS state, for a model chiral D–B–A system undergoing hopping mediated charge recombination, where the intermediate CS* state has a lifetime of ~10 ns (the complete set of model parameters are given in the figure caption). We have previously shown how photo-generated CS states formed by hopping become spin-polarized.[7] Given this, we set the initial CS state spin density operator to be the spin polarized state that would be formed if the initial photo-excitation generates the CS* state in the $\hat{\sigma}_\theta = |\psi_\theta\rangle\langle\psi_\theta|$ state, as predicted by the theory in Ref. 7. Under the assumption that the initial CS state formation is very fast compared to charge recombination, the initial density operator is given by[7]

$$\hat{\sigma}_{CS}(0) \approx k_b \int_0^\infty dt\, e^{\mathcal{L}_{CS^\star} t}\hat{\sigma}_\theta = -\frac{k_b}{\phi_{CS}}\mathcal{L}^{-1}_{CS^\star}\hat{\sigma}_\theta, \tag{21}$$

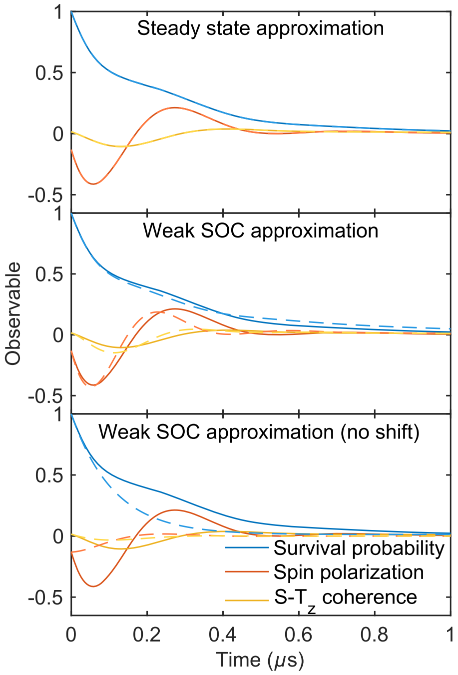

FIG. 2. Dynamics of the hopping model, calculated with the full set of density operator equations (solid lines) and various levels of approximation for the reaction superoperator (dashed lines). In this example, $J = 1000$ mT, $\delta\epsilon = -0.98J$, $k_\mathrm{f} = 100\ \mu\mathrm{s}^{-1}$, $k_\mathrm{b} = 100k_\mathrm{f}$, and $k_\mathrm{CR} = 10k_\mathrm{f}$, and $\theta = 0.02$, and the CS state is initialized in a spin-polarized initial state, as defined by Eq. (21).

where ϕ_CS is the CS state quantum yield, given by $\phi_\mathrm{CS} = -\mathrm{Tr}[k_\mathrm{b}\mathcal{L}^{-1}_{\mathrm{CS}^*}\hat{\sigma}_\theta]$. For the parameters chosen here, this produces a state which has ∼−12% initial spin polarization. For this example, we have calculated the spin dynamics for the full model, Eqs. (8) and (9), for the full steady state approximation, Eq. (11), and for the weak spin–orbit coupling reaction superoperator obtained in Appendix B, and neglecting the weak spin–orbit coupling contribution to the $\delta\hat{H}$ [i.e., setting $\delta\epsilon^{(1)}_{\mathrm{ST}_z}$ in Eq. (B20) to zero].

In the top panel of Fig. 2, we show the CS survival probability (blue), $p(t) = \mathrm{Tr}[\hat{\sigma}_\mathrm{CS}(t)]$, and spin polarization (red), $\langle \Delta S_z \rangle$, and spin coherence (gold), $\langle \Pi_{\mathrm{ST}_z} \rangle$, for the full model, Eqs. (8) and (9), (solid lines) and for the full effective reaction superoperator, Eq. (11), (dashed lines). In this example, both spin coherence and spin polarization are generated transiently by the hopping process, and oscillations in these quantities induce oscillations in the CS state decay rate. We also see that the net spin-polarization generated in the CS state eventually decays to zero. This is because all spin-polarized states are coupled by effective interactions in $\delta\hat{H}$, which means that the CS state fully decays, leaving zero net spin-polarization. We see that the full model result and effective reaction superoperator obtained with the steady-state approximation agree to graphical accuracy, even in this model with physically reasonable parameters where the frequency associated with $2J$ is significantly faster than the decay rate of the intermediate state. In the middle panel, we compare the full model (solid lines) and the weak spin–orbit coupling reaction superoperator, Eq. (B7) (dashed lines), which recovers most of the population and spin-polarization dynamics, but is not quantitatively accurate for this example. In the bottom panel of Fig. 2, we show results for the same calculation, neglecting $\mathcal{O}(\sin\theta)$ contributions to $\delta\hat{H}$ in the weak spin–orbit coupling reaction superoperator, Eq. (B7). This approximation fails to capture the spin polarization dynamics accurately in this example, which demonstrates that the emergent spin polarization in the CS state is primarily generated by the augmentation of coherent spin dynamics, rather than spin-selective recombination.

To further test the importance of $\delta\hat{H}$, we have calculated the decay rate, $k(t) = -\dot{p}(t)/p(t)$, the spin polarization and spin coherence for the same model for a range of exchange couplings J, and $\delta\epsilon$ values in the intermediate state, as shown in Fig. 3. In each case, we calculate the full spin dynamics of the CS state (solid lines), which agree to graphical accuracy with the full steady-state approximation results, and compare these to the dynamics with the steady-state approximation reaction superoperator with $\delta\hat{H} = 0$ (dashed lines). We see that across a range of J values (with $\delta\epsilon = -0.98J$ in each case), $\delta\hat{H}$ cannot be neglected, even when the full steady-state approximation for the reaction operator and the decoherence term are used. This approximation can even be qualitatively wrong, for example, when $\delta\hat{H}$ is neglected in the $J = 100$ mT and $J = 1000$ mT examples, the sign of the predicted spin polarization is wrong. We also see that even when $\delta\hat{H}$ is set to zero, the decoherence contributions to $\mathcal{K}$ destroy the long-lived spin polarization. Overall, these tests show that both the reaction operator and the Hamiltonian shift play a significant role in determining the spin polarization dynamics and survival probability of the CS state in this example, and the Hamiltonian shift $\delta\hat{H}$ cannot simply be ignored, so, the full reaction superoperator should always be used in calculations.

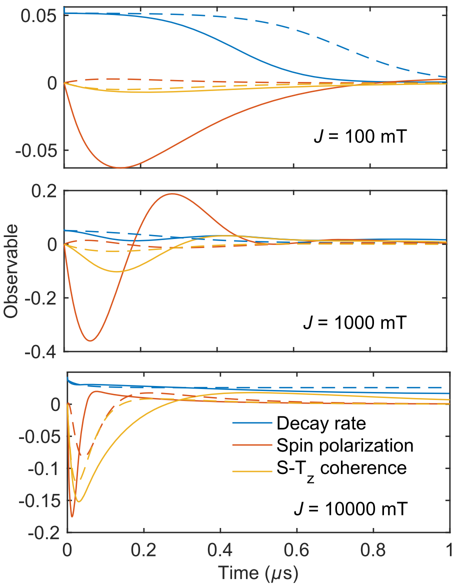

FIG. 3. Dynamics of the hopping model, calculated with the full set of density operator equations (solid lines) and the full steady state reaction superoperator, with $\delta\hat{H} = 0$ (dashed lines). In this example, J is varied, and in each case, $\delta\epsilon = -0.98J$, $k_\mathrm{f} = 100\ \mu\mathrm{s}^{-1}$, $k_\mathrm{b} = 100k_\mathrm{f}$, $k_\mathrm{CR} = 10k_\mathrm{f}$, and $\theta = 0.02$.

For simplicity in these tests, we have ignored any coherent spin dynamics in the CS state other than those generated transiently in the hopping process. However, in a real chiral D–B–A molecule, dipolar and superexchange electron spin couplings would exist in the CS state, as well as hyperfine couplings to nuclear spins. For the model calculations performed here, with physically motivated parameter choices, $\delta\hat{H}$ produces electron spin dynamics on roughly a 200 ns time-scale, with a corresponding energy scale of ~0.05 mT $\hbar\gamma_e$, the effect of which can be measured experimentally even in the presence of competing interactions, as is observed, for example, in the low magnetic field effect.[32–35] However, in some systems, other spin–spin interactions could well dominate over $\delta\hat{H}$, and disentangling $\delta\hat{H}$ effects from these other spin–spin interactions would require detailed modeling of the system of interest.

IV. CONCLUSIONS

In this work, we have derived a description of spin-selective electron transfer in chiral donor–bridge–acceptor systems through the reaction superoperator formalism. We have obtained expressions for this superoperator, applicable in both the superexchange and hopping regimes, for the recombination process. The form of the reaction superoperator is very simple in the superexchange limit, where it is not selective for spin polarization. However, in the hopping mediated limit, the reaction superoperator becomes more complicated, and we have found that the recombination is selective for both spin-polarization and spin-coherence in this case. The spin polarization selectivity should be understood as arising from the spin-polarization being generated in molecules initially in non-reactive spin states, which is transferred back to the CS state in reverse-hopping. We also find that spin-polarization selectivity emerges only when the intermediate charge separated state is sufficiently long-lived and when an exchange coupling in this state is large enough to generate spin polarization in molecules in non-reactive spin states. We have also found that spin polarization selectivity can be reversed relative to the chirality induced spin polarization generated by photo-excitation, and that the selectivity depends on the phases couplings between bridge orbitals and the orbitals in the ground state and the excited precursor. This inverse spin polarization selectivity of formation recombination could have some biological function, for example, in magnetoreception,[8,36,37] or in hindering reverse electron transfer in photosynthetic reaction centers.[18,38]

Numerical tests have shown that in hopping mediated charge recombination, chirality dependent shifts in the spin Hamiltonian, which are induced by transient dynamics in the intermediate state, also play an essential role in determining the survival probability and spin polarization in the charge separated state. This shift Hamiltonian mixes all spin-polarized states, thereby destroying the long-lived spin polarization in the CS state. In order to accurately describe the dynamics of charge recombination in chiral molecules, it is clearly necessary to account for both spin-selectivity in the reaction and augmentation of the coherent dynamics by the recombination process. It is important to note that the theory proposed here is not fully consistent with the phenomenological treatments of CISS that have been proposed recently,[8] and that have been used to investigate the role of CISS in avian magnetoreception.[8,36,37] Although the theory that we have presented does not have the simplicity of this phenomenological treatment, it is derived from a physically reasonable model, and all parameters appearing in the theory (such as forward and backward hopping rates) can, in principle, be measured experimentally or calculated using computational approaches. Experimental and computational studies suggest that hopping mediated charge recombination may play a role in avian magnetoreception,[39,40] and with the theory presented here, it would be possible to rigorously study chirality-mediated spin effects in magnetoreception. The spin density operator framework used here can be extended straightforwardly to include other important physics of spin-correlated charge separated states that are necessary to understand real systems, such as hyperfine coupling effects and spin relaxation.[5,41–46] We anticipate that this framework for understanding spin-selective charge recombination in chiral systems will be useful in numerous contexts involving molecular CISS, such as in devising systems exploiting CISS for quantum information science and in studies of CISS effects in biological electron transfer.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Thomas P. Fay: Conceptualization (lead); Formal analysis (lead); Investigation (lead); Writing – original draft (lead); Writing – review & editing (equal). **David T. Limmer**: Formal analysis (supporting); Funding acquisition (lead); Supervision (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

APPENDIX A: EFFECTIVE HAMILTONIAN THEORY FOR SUPEREXCHANGE ELECTRON TRANSFER

Here, we derive the effective Hamiltonian, Eq. (7), starting from the full model electronic state Hamiltonian given by Eq. (6). We assume that the couplings Λ_{DB}, V_{DB}, and V_{BA} are small and that $E_{\mathrm{CS}^\star} \gg E_{\mathrm{S}_0}, E_{\mathrm{CS},\ominus}$. In this case, the eigenvectors of $\hat{H} = \hat{H}_{\mathrm{DBA}}$ can be partitioned into two approximate subspaces, one spanned by the high energy CS* states and one spanned by the low energy CS and S$_0$ states. With this observation, we can derive an approximate form for the electronic Hamiltonian within the low-energy subspace. We first define a projection operator onto the low- energy subspace

$\hat{P} = |\mathrm{S}_0\rangle\langle\mathrm{S}_0| + \sum_\Theta |\mathrm{CS},\Theta\rangle\langle\mathrm{CS},\Theta|$, and its complement $\hat{Q} = 1 - \hat{P}$. We project the electronic energy eigenstate equation $\hat{H}|\Psi\rangle = E|\Psi\rangle$ to obtain equations for $|\Psi\rangle$ in the $\hat{P}$ and $\hat{Q}$ projected spaces,[47]

$$E\hat{P}|\Psi\rangle = \hat{P}\hat{H}\hat{P}|\Psi\rangle + \hat{P}\hat{H}\hat{Q}|\Psi\rangle, \tag{A1}$$

$$E\hat{Q}|\Psi\rangle = \hat{Q}\hat{H}\hat{P}|\Psi\rangle + \hat{Q}\hat{H}\hat{Q}|\Psi\rangle. \tag{A2}$$

Solving the equation for $\hat{Q}|\Psi\rangle$ and substituting this into the equation for $\hat{P}|\Psi\rangle$ yields an effective equation for $\hat{P}|\Psi\rangle$,

$$E\hat{P}|\Psi\rangle = [\hat{P}\hat{H}\hat{P} + \hat{P}\hat{H}\hat{Q}(E - \hat{Q}\hat{H}\hat{Q})^{-1}\hat{Q}\hat{H}\hat{P}]\hat{P}|\Psi\rangle. \tag{A3}$$

The effective Hamiltonian appearing on the right-hand side of this equation is dependent on E, but by exploiting the large separation between the low- and high-energy states, we can replace $(E - \hat{Q}\hat{H}\hat{Q})^{-1} \to (\bar{E} - \hat{Q}\hat{H}\hat{Q})^{-1}$, where $\bar{E}$ is the mean energy of the CS and S_0 states. With this approximation, and by noting that $\hat{P}\hat{H}\hat{P}$, $\hat{Q}\hat{H}\hat{Q}$, and $\hat{P}\hat{H}\hat{Q}$, with $\hat{H} = \hat{H}_{\mathrm{DBA}}$, can be written as

$$\hat{P}\hat{H}\hat{P} = E_{\mathrm{S}_0}|\mathrm{S}_0\rangle\langle\mathrm{S}_0| + \sum_\Theta E_{\mathrm{CS},\Theta}|\mathrm{CS},\Theta\rangle\langle\mathrm{CS},\Theta|, \tag{A4}$$

$$\hat{Q}\hat{H}\hat{Q} = \sum_\Theta E_{\mathrm{CS}^\star,\Theta}|\mathrm{CS}^\star,\Theta\rangle\langle\mathrm{CS}^\star,\Theta|, \tag{A5}$$

$$\begin{aligned}\hat{P}\hat{H}\hat{Q} = {} & \sum_\Theta V_{\mathrm{BA}}|\mathrm{CS},\Theta\rangle\langle\mathrm{CS}^\star,\Theta| \\ & + V_{\mathrm{DB}}|\mathrm{S}_0\rangle\langle\mathrm{CS}^\star,\mathrm{S}| - \frac{i\Lambda_{\mathrm{DB}}}{2}|\mathrm{S}_0\rangle\langle\mathrm{CS}^\star,\mathrm{T}_z|,\end{aligned} \tag{A6}$$

$$\hat{Q}\hat{H}\hat{P} = (\hat{P}\hat{H}\hat{Q})^\dagger, \tag{A7}$$

we straightforwardly obtain Eq. (7) for $\hat{H}_{\mathrm{DBA,eff}}$, where the energy level shifts in Eq. (7) are given by

$$\delta E_{\mathrm{S}_0} = \frac{V_{\mathrm{DB}}^2}{\bar{E} - E_{\mathrm{CS}^\star,\mathrm{S}}} + \frac{\Lambda_{\mathrm{DB}}^2}{4(\bar{E} - E_{\mathrm{CS}^\star,\mathrm{T}_z})}, \tag{A8}$$

$$\delta E_{\mathrm{CS},\Theta} = \frac{V_{\mathrm{BA}}^2}{\bar{E} - E_{\mathrm{CS}^\star,\Theta}}. \tag{A9}$$

APPENDIX B: THE WEAK SOC REACTION OPERATOR

In order to derive the weak spin–orbit coupling reaction superoperator, we partition $\mathcal{L}_{\mathrm{CS}^\star}$ into a sum of a reference term, $\mathcal{L}_{\mathrm{d}}$, which is diagonal in the singlet–triplet basis, and a term which couples the singlet and triplet states, $\mathcal{L}_{\mathrm{c}}$. The diagonal term is given by

$$\mathcal{L}_{\mathrm{d}} = -\left\{\frac{k_{\mathrm{S}}}{2}\hat{P}_{\mathrm{S}} + \frac{k_{\mathrm{T}_z}}{2}\hat{P}_{\mathrm{T}_z} + \frac{k_{\mathrm{b}}}{2},\ \cdot\ \right\} - i[\epsilon_{\mathrm{S}}\hat{P}_{\mathrm{S}} + \epsilon_{\mathrm{T}_z}\hat{P}_{\mathrm{T}_z},\ \cdot\ ], \tag{B1}$$

where the effective rate constants and energies are given by

$$k_{\mathrm{S}} = k_{\mathrm{CR}}\cos^2\theta, \tag{B2}$$

$$k_{\mathrm{T}_z} = k_{\mathrm{CR}}\sin^2\theta, \tag{B3}$$

$$\epsilon_{\mathrm{S}} = 2J + \delta\epsilon\cos^2\theta, \tag{B4}$$

$$\epsilon_{\mathrm{T}_z} = \delta\epsilon\sin^2\theta. \tag{B5}$$

The coupling term is given by

$$\mathcal{L}_{\mathrm{c}} = -\left\{\frac{k_{\mathrm{CR}}}{2}\sin(2\theta)\hat{\Pi}_{\mathrm{ST}_z},\ \cdot\ \right\} - i[\delta\epsilon\sin(2\theta)\hat{\Pi}_{\mathrm{ST}_z},\ \cdot\ ]. \tag{B6}$$

We can expand the reaction superoperator to first-order in the coupling term, which gives the following expressions for the reaction superoperator:

$$\mathcal{K} \approx \mathcal{K}^{(0)} + \mathcal{K}^{(1)}, \tag{B7}$$

$$\mathcal{K}^{(0)} = -k_{\mathrm{f}}(1 + k_{\mathrm{b}}\mathcal{L}_{\mathrm{d}}^{-1}), \tag{B8}$$

$$\mathcal{K}^{(1)} = k_{\mathrm{f}}k_{\mathrm{b}}\mathcal{L}_{\mathrm{d}}^{-1}\mathcal{L}_{\mathrm{c}}\mathcal{L}_{\mathrm{d}}^{-1}. \tag{B9}$$

The $\mathcal{K}^{(0)}$ is given by

$$\begin{aligned}\mathcal{K}^{(0)} = {} & -\left\{\frac{\tilde{k}_{\mathrm{S}}^{(0)}}{2}\hat{P}_{\mathrm{S}} + \frac{\tilde{k}_{\mathrm{T}_z}^{(0)}}{2}\hat{P}_{\mathrm{T}_z},\ \cdot\ \right\} - i\left[\tilde{\epsilon}_{\mathrm{S}}^{(0)}\hat{P}_{\mathrm{S}} + \tilde{\epsilon}_{\mathrm{T}_z}^{(0)}\hat{P}_{\mathrm{T}_z},\ \cdot\ \right] \\ & + \gamma_{\mathrm{S}}^{(0)}\left(\hat{P}_{\mathrm{S}}\ \cdot\ \hat{P}_{\mathrm{S}} - \frac{1}{2}\{\hat{P}_{\mathrm{S}},\ \cdot\ \}\right) \\ & + \gamma_{\mathrm{T}_z}^{(0)}\left(\hat{P}_{\mathrm{T}_z}\ \cdot\ \hat{P}_{\mathrm{T}_z} - \frac{1}{2}\{\hat{P}_{\mathrm{T}_z},\ \cdot\ \}\right),\end{aligned} \tag{B10}$$

where the effective rate constants are given by

$$\tilde{k}_{\mathrm{S}}^{(0)} = \frac{k_{\mathrm{f}}k_{\mathrm{S}}}{k_{\mathrm{S}} + k_{\mathrm{b}}}, \tag{B11}$$

$$\tilde{k}_{\mathrm{T}_z}^{(0)} = \frac{k_{\mathrm{f}}k_{\mathrm{T}_z}}{k_{\mathrm{T}_z} + k_{\mathrm{b}}}, \tag{B12}$$

the effective energy shifts are given by

$$\begin{aligned}\tilde{\epsilon}_{\mathrm{S}}^{(0)} = 2k_{\mathrm{f}}k_{\mathrm{b}}\Bigg(& \frac{\epsilon_{\mathrm{S}} - \epsilon_{\mathrm{T}_z}}{(2k_{\mathrm{b}} + k_{\mathrm{S}} + k_{\mathrm{T}_z})^2 + 4(\epsilon_{\mathrm{S}} - \epsilon_{\mathrm{T}_z})^2} \\ & + \frac{\epsilon_{\mathrm{S}}}{(2k_{\mathrm{b}} + k_{\mathrm{S}})^2 + 4\epsilon_{\mathrm{S}}^2}\Bigg),\end{aligned} \tag{B13}$$

$$\begin{aligned}\tilde{\epsilon}_{\mathrm{T}_z}^{(0)} = 2k_{\mathrm{f}}k_{\mathrm{b}}\Bigg(& \frac{\epsilon_{\mathrm{T}_z} - \epsilon_{\mathrm{S}}}{(2k_{\mathrm{b}} + k_{\mathrm{S}} + k_{\mathrm{T}_z})^2 + 4(\epsilon_{\mathrm{S}} - \epsilon_{\mathrm{T}_z})^2} \\ & + \frac{\epsilon_{\mathrm{T}_z}}{(2k_{\mathrm{b}} + k_{\mathrm{T}_z})^2 + 4\epsilon_{\mathrm{T}_z}^2}\Bigg),\end{aligned} \tag{B14}$$

and the decoherence rates are given by

$$\gamma_{\mathrm{S}}^{(0)} = k_{\mathrm{f}} - \frac{k_{\mathrm{f}}k_{\mathrm{b}}(2k_{\mathrm{b}} + k_{\mathrm{T}_z} + k_{\mathrm{S}})}{(2k_{\mathrm{b}} + k_{\mathrm{T}_z} + k_{\mathrm{S}})^2 + 4(\epsilon_{\mathrm{T}_z} - \epsilon_{\mathrm{S}})^2} - \frac{k_{\mathrm{f}}k_{\mathrm{b}}(2k_{\mathrm{b}} + k_{\mathrm{S}})}{(2k_{\mathrm{b}} + k_{\mathrm{S}})^2 + 4\epsilon_{\mathrm{S}}^2}, \tag{B15}$$

$$\gamma_{\mathrm{T}_z}^{(0)} = k_{\mathrm{f}} - \frac{k_{\mathrm{f}}k_{\mathrm{b}}(2k_{\mathrm{b}} + k_{\mathrm{S}} + k_{\mathrm{T}_z})}{(2k_{\mathrm{b}} + k_{\mathrm{S}} + k_{\mathrm{T}_z})^2 + 4(\epsilon_{\mathrm{S}} - \epsilon_{\mathrm{T}_z})^2} - \frac{k_{\mathrm{f}}k_{\mathrm{b}}(2k_{\mathrm{b}} + k_{\mathrm{T}_z})}{(2k_{\mathrm{b}} + k_{\mathrm{T}_z})^2 + 4\epsilon_{\mathrm{T}_z}^2}. \tag{B16}$$

Ignoring any decoherence corrections to $\mathcal{K}^{(1)}$, $\mathcal{K}^{(1)}$ can be written as

$$\mathcal{K}^{(1)} \approx -\left\{ \frac{\tilde{k}_z^{(1)}}{2}\Delta\hat{S}_z + \frac{\tilde{k}_{\mathrm{ST}_z}^{(1)}}{2}\hat{\Pi}_{\mathrm{ST}_z}, \cdot \right\} - i\left[\delta\tilde{\epsilon}_{\mathrm{ST}_z}^{(1)}\hat{\Pi}_{\mathrm{ST}_z}, \cdot\right], \tag{B17}$$

where the spin polarization selective rate is given by

$$\tilde{k}_z^{(1)} = -\frac{2\sin(2\theta)k_\mathrm{f}k_\mathrm{b}(2k_\mathrm{b}+k_\mathrm{S}+k_{\mathrm{T}_z})(\delta\epsilon(k_\mathrm{S}-k_{\mathrm{T}_z})+k_\mathrm{CR}(\epsilon_{\mathrm{T}_z}-\epsilon_\mathrm{S}))}{(k_\mathrm{b}+k_\mathrm{S})(k_\mathrm{b}+k_{\mathrm{T}_z})\left((2k_\mathrm{b}+k_\mathrm{S}+k_{\mathrm{T}_z})^2+4(\epsilon_\mathrm{S}-\epsilon_{\mathrm{T}_z})^2\right)}, \tag{B18}$$

the spin coherence selective rate is given by

$$\tilde{k}_{\mathrm{ST}_z}^{(1)} = \frac{\sin(2\theta)k_\mathrm{f}k_\mathrm{b}(4k_\mathrm{CR}k_\mathrm{b}(k_\mathrm{S}+k_{\mathrm{T}_z}+k_\mathrm{b})+k_\mathrm{CR}(k_\mathrm{S}+k_{\mathrm{T}_z})^2+4\delta\epsilon(k_\mathrm{S}-k_{\mathrm{T}_z})(\epsilon_\mathrm{S}-\epsilon_{\mathrm{T}_z}))}{(k_\mathrm{b}+k_\mathrm{S})(k_\mathrm{b}+k_{\mathrm{T}_z})\left((2k_\mathrm{b}+k_\mathrm{S}+k_{\mathrm{T}_z})^2+4(\epsilon_\mathrm{S}-\epsilon_{\mathrm{T}_z})^2\right)}, \tag{B19}$$

and the Hamiltonian correction term is given by

$$\begin{aligned}\delta\tilde{\epsilon}_{\mathrm{ST}_z}^{(1)} = \frac{2}{3}\sin(2\theta)k_\mathrm{f}k_\mathrm{b}\Bigg(&\frac{2((2k_\mathrm{b}+k_{\mathrm{T}_z})(2\delta\epsilon k_\mathrm{b}+\delta\epsilon k_\mathrm{S}-k_\mathrm{CR}\epsilon_\mathrm{S})-\epsilon_{\mathrm{T}_z}(2k_\mathrm{CR}k_\mathrm{b}+k_\mathrm{CR}k_\mathrm{S}+4\delta\epsilon\epsilon_\mathrm{S}))}{\left((2k_\mathrm{b}+k_\mathrm{S})^2+4\epsilon_\mathrm{S}^2\right)\left((2k_\mathrm{b}+k_{\mathrm{T}_z})^2+4\epsilon_{\mathrm{T}_z}^2\right)}\\ &+\frac{4\delta\epsilon k_\mathrm{b}^2+4\delta\epsilon k_\mathrm{b}(k_\mathrm{S}+k_{\mathrm{T}_z})+\delta\epsilon k_\mathrm{S}^2+k_\mathrm{S}(-k_\mathrm{CR}\epsilon_\mathrm{S}+2\delta\epsilon k_{\mathrm{T}_z}+k_\mathrm{CR}\epsilon_{\mathrm{T}_z})+k_{\mathrm{T}_z}(k_\mathrm{CR}\epsilon_\mathrm{S}+\delta\epsilon k_{\mathrm{T}_z}-k_\mathrm{CR}\epsilon_{\mathrm{T}_z})}{(k_\mathrm{b}+k_\mathrm{S})(k_\mathrm{b}+k_{\mathrm{T}_z})\left((2k_\mathrm{b}+k_\mathrm{S}+k_{\mathrm{T}_z})^2+4(\epsilon_\mathrm{S}-\epsilon_{\mathrm{T}_z})^2\right)}\Bigg).\end{aligned} \tag{B20}$$

REFERENCES

[1] C. D. Aiello, J. M. Abendroth, M. Abbas, A. Afanasev, S. Agarwal, A. S. Banerjee, D. N. Beratan, J. N. Belling, B. Berche, A. Botana, J. R. Caram, G. L. Celardo, G. Cuniberti, A. Garcia-Etxarri, A. Dianat, I. Diez-Perez, Y. Guo, R. Gutierrez, C. Herrmann, J. Hihath, S. Kale, P. Kurian, Y.-C. Lai, T. Liu, A. Lopez, E. Medina, V. Mujica, R. Naaman, M. Noormandipour, J. L. Palma, Y. Paltiel, W. Petuskey, J. C. Ribeiro-Silva, J. J. Saenz, E. J. G. Santos, M. Solyanik-Gorgone, V. J. Sorger, D. M. Stemer, J. M. Ugalde, A. Valdes-Curiel, S. Varela, D. H. Waldeck, M. R. Wasielewski, P. S. Weiss, H. Zacharias, and Q. H. Wang, "A chirality-based quantum leap," ACS Nano **16**, 4989–5035 (2022); arXiv:2009.00136.

[2] A. Privitera, D. Faccio, D. Giuri, D. Genovese, F. Tassinari, L. Mummolo, M. Chiesa, C. Fontanesi, E. Salvadori, and A. Cornia, C. Tomasini, and R. Sessoli, "Challenges in the direct detection of chirality-induced spin selectivity: Investigation of foldamer-based donor/acceptor dyads," chemRxiv (2022).

[3] F. Evers, A. Aharony, N. Bar-Gill, O. Entin-Wohlman, P. Hedegård, O. Hod, P. Jelinek, G. Kamieniarz, M. Lemeshko, K. Michaeli, V. Mujica, R. Naaman, Y. Paltiel, S. Refaely-Abramson, O. Tal, J. Thijssen, M. Thoss, J. M. van Ruitenbeek, L. Venkataraman, D. H. Waldeck, B. Yan, and L. Kronik, "Theory of chirality induced spin selectivity: Progress and challenges," Adv. Mater. **34**, 2106629 (2022); arXiv:2108.09998.

[4] L. A. Völker, K. Herb, E. Janitz, C. L. Degen, and J. M. Abendroth, "Towards quantum sensing of chiral-induced spin selectivity: Probing donor-bridge-acceptor molecules with NV centers in diamond," arXiv:2302.01725 (2023).

[5] A. Chiesa, M. Chizzini, E. Garlatti, E. Salvadori, F. Tacchino, P. Santini, I. Tavernelli, R. Bittl, M. Chiesa, R. Sessoli, and S. Carretta, "Assessing the nature of chiral-induced spin-selectivity by magnetic resonance," J. Phys. Chem. Lett. **12**(27), 6341–6341 (2021).

[6] A. Privitera, E. Macaluso, A. Chiesa, A. Gabbani, D. Faccio, D. Giuri, M. Briganti, N. Giaconi, F. Santanni, N. Jarmouni, L. Poggini, M. Mannini, M. Chiesa, C. Tomasini, F. Pineider, E. Salvadori, S. Carretta, and R. Sessoli, "Direct detection of spin polarization in photoinduced charge transfer through a chiral bridge," Chem. Sci. **13**, 12208–12218 (2022).

[7] T. P. Fay and D. T. Limmer, "Origin of chirality induced spin selectivity in photoinduced electron transfer," Nano Lett. **21**, 6696–6702 (2021); arXiv:2106.06554.

[8] J. Luo and P. J. Hore, "Chiral-induced spin selectivity in the formation and recombination of radical pairs: Cryptochrome magnetoreception and EPR detection," New J. Phys. **23**, 043032 (2021).

[9] R. Naaman, Y. Paltiel, and D. H. Waldeck, "Chiral molecules and the spin selectivity effect," J. Phys. Chem. Lett. **11**, 3660–3666 (2020).

[10] D. H. Waldeck, R. Naaman, and Y. Paltiel, "The spin selectivity effect in chiral materials," APL Mater. **9**, 040902 (2021).

[11] A. C. Aragonès, E. Medina, M. Ferrer-Huerta, N. Gimeno, M. Teixidó, J. L. Palma, N. Tao, J. M. Ugalde, E. Giralt, I. Díez-Pérez, and V. Mujica, "Measuring the spin-polarization power of a single chiral molecule," Small **13**, 1602519 (2017).

[12] S. Naskar, V. Mujica, and C. Herrmann, "Chiral-induced spin selectivity and non-equilibrium spin accumulation in molecules and interfaces: A first-principles study," J. Phys. Chem. Lett. **14**, 694–701 (2023).

[13] R. Naaman and D. H. Waldeck, "Spintronics and chirality: Spin selectivity in electron transport through chiral molecules," Annu. Rev. Phys. Chem. **66**, 263–281 (2015).

[14] M. R. Wasielewski, "Light-driven spin chemistry for quantum information science," Phys. Today **76**(3), 28–34 (2023).

[15] T. P. Fay, "Chirality-induced spin coherence in electron transfer reactions," J. Phys. Chem. Lett. **12**, 1407–1412 (2021); arXiv:2101.03104.

[16] S. S. Chandran, Y. Wu, H.-H. Teh, D. H. Waldeck, and J. E. Subotnik, "Electron transfer and spin–orbit coupling: Can nuclear motion lead to spin selective rates?," J. Chem. Phys. **156**, 174113 (2022).

[17] S. S. Chandran, Y. Wu, and J. E. Subotnik, "Effect of Duschinskii rotations on spin-dependent electron transfer dynamics," J. Phys. Chem. A **126**, 9535–9552 (2022); arXiv:2208.13378.

[18] I. Carmeli, K. S. Kumar, O. Heifler, C. Carmeli, and R. Naaman, "Spin selectivity in electron transfer in photosystem I," Angew. Chem., Int. Ed. **53**, 8953–8958 (2014).

[19] M. J. Junge, M. A. Kordan, and E. T. Chernick, "Synthesis of chiral donor–acceptor dyes to study electron transfer across a chiral bridge," J. Org. Chem. **85**, 13793–13807 (2020).

[20] M. R. Wasielewski, "Energy, charge, and spin transport in molecules and self-assembled nanostructures inspired by photosynthesis," J. Org. Chem. **71**, 5051–5066 (2006).

[21] T. Mani, "Molecular qubits based on photogenerated spin-correlated radical pairs for quantum sensing," Chem. Phys. Rev. **3**, 021301 (2022).

[22] R. Haberkorn, "Density matrix description of spin-selective radical pair reactions," Mol. Phys. **32**, 1491–1493 (1976).

[23] K. L. Ivanov, M. V. Petrova, N. N. Lukzen, and K. Maeda, "Consistent treatment of spin-selective recombination of a radical pair confirms the Haberkorn approach," J. Phys. Chem. A **114**, 9447–9455 (2010).

[24] K. Maeda, P. Liddell, D. Gust, and P. J. Hore, "Spin-selective recombination reactions of radical pairs: Experimental test of validity of reaction operators," J. Chem. Phys. **139**, 234309 (2013).

[25] T. P. Fay, L. P. Lindoy, and D. E. Manolopoulos, "Spin-selective electron transfer reactions of radical pairs: Beyond the Haberkorn master equation," J. Chem. Phys. **149**, 064107 (2018); arXiv:1808.03211.

[26] V. May and O. Kühn, *Charge and Energy Transfer Dynamics in Molecular Systems* (Wiley-VCH Verlag GmbH and Co. KGaA, 2000).

[27] R. A. Marcus, "On the theory of oxidation-reduction reactions involving electron transfer. I," J. Chem. Phys. **24**, 966–978 (1956).

[28] N. S. Hush, "Adiabatic rate processes at electrodes. I. Energy-charge relationships," J. Chem. Phys. **28**, 962–972 (1958).

[29] Y. Hu and S. Mukamel, "Tunneling versus sequential long-range electron transfer: Analogy with pump–probe spectroscopy," J. Chem. Phys. **91**, 6973–6988 (1989).

[30] E. G. Petrov, Y. V. Shevchenko, V. I. Teslenko, and V. May, "Nonadiabatic donor–acceptor electron transfer mediated by a molecular bridge: A unified theoretical description of the superexchange and hopping mechanism," J. Chem. Phys. **115**, 7107–7122 (2001).

[31] M. T. Colvin, A. B. Ricks, A. M. Scott, D. T. Co, and M. R. Wasielewski, "Intersystem crossing involving strongly spin exchange-coupled radical ion pairs in donor–bridge–acceptor molecules," J. Phys. Chem. A **116**, 1923–1930 (2012).

[32] C. A. Hamilton, J. P. Hewitt, K. A. McLauchlan, and U. E. Steiner, "High resolution studies of the effects of magnetic fields on chemical reactions," Mol. Phys. **65**, 423–438 (1988).

[33] S. N. Batchelor, C. W. M. Kay, K. A. McLauchlan, and I. A. Shkrob, "Time-resolved and modulation methods in the study of the effects of magnetic fields on the yields of free-radical reactions," J. Phys. Chem. **97**, 13250–13258 (1993).

[34] A. M. Lewis, T. P. Fay, D. E. Manolopoulos, C. Kerpal, S. Richert, and C. R. Timmel, "On the low magnetic field effect in radical pair reactions," J. Chem. Phys. **149**, 034103 (2018).

[35] C. R. Timmel and K. B. Henbest, "A study of spin chemistry in weak magnetic fields," Philos. Trans. R. Soc., A **362**, 2573–2589 (2004).

[36] Y. Tiwari and V. S. Poonia, "Role of chiral-induced spin selectivity in the radical pair mechanism of avian magnetoreception," Phys. Rev. E **106**, 064409 (2022).

[37] Y. Tiwari and V. S. Poonia, "Chiral-induced spin selectivity augments quantum coherence in avian compass," arXiv:2212.04073 (2022).

[38] R. Naaman, Y. Paltiel, and D. H. Waldeck, "Chiral induced spin selectivity and its implications for biological functions," Annu. Rev. Biophys. **51**, 99–114 (2022).

[39] J. Xu, L. E. Jarocha, T. Zollitsch, M. Konowalczyk, K. B. Henbest, S. Richert, M. J. Golesworthy, J. Schmidt, V. Déjean, D. J. C. Sowood, M. Bassetto, J. Luo, J. R. Walton, J. Fleming, Y. Wei, T. L. Pitcher, G. Moise, M. Herrmann, H. Yin, H. Wu, R. Bartölke, S. J. Käsehagen, S. Horst, G. Dautaj, P. D. F. Murton, A. S. Gehrckens, Y. Chelliah, J. S. Takahashi, K.-W. Koch, S. Weber, I. A. Solov'yov, C. Xie, S. R. Mackenzie, C. R. Timmel, H. Mouritsen, and P. J. Hore, "Magnetic sensitivity of cryptochrome 4 from a migratory songbird," Nature **594**, 535–540 (2021).

[40] .S. Y. Wong, Y. Wei, H. Mouritsen, I. A. Solov'yov, and P. J. Hore, "Cryptochrome magnetoreception: Four tryptophans could be better than three," J. R. Soc. Interface **18**, 20210601 (2021).

[41] U. E. Steiner and T. Ulrich, "Magnetic field effects in chemical kinetics and related phenomena," Chem. Rev. **89**, 51–147 (1989).

[42] M. P. Nicholas, E. Eryilmaz, F. Ferrage, D. Cowburn, and R. Ghose, "Nuclear spin relaxation in isotropic and anisotropic media," Prog. Nucl. Magn. Reson. Spectrosc. **57**, 111–158 (2010).

[43] T. P. Fay, L. P. Lindoy, and D. E. Manolopoulos, "Electron spin relaxation in radical pairs: Beyond the Redfield approximation," J. Chem. Phys. **151**, 154117 (2019).

[44] R. H. Keens and D. R. Kattnig, "Monte-Carlo wavefunction approach for the spin dynamics of recombining radicals," New J. Phys. **22**, 083064 (2020); arXiv:2005.04417.

[45] T. P. Fay, L. P. Lindoy, and D. E. Manolopoulos, "Spin relaxation in radical pairs from the stochastic Schrödinger equation," J. Chem. Phys. **154**, 084121 (2021); arXiv:2102.13430.

[46] L. P. Lindoy, T. P. Fay, and D. E. Manolopoulos, "Quantum mechanical spin dynamics of a molecular magnetoreceptor," J. Chem. Phys. **152**, 164107 (2020).

[47] F. Mila and K. P. Schmidt, "Strong-coupling expansion and effective Hamiltonians," in *Introduction to Frustrated Magnetism*, Springer Series in Solid-State Sciences Vol. 164, edited by C. Lacroix, P. Mendels, and F. Mila (Springer, Berlin, Heidelberg, 2011), pp. 537–559.