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Quintet formation, exchange fluctuations, and the role of stochastic resonance in singlet fission

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Singlet fission describes the spin-conserving production of two triplet excitons from one singlet exciton. The existence of a spin-2 (quintet) triplet-pair state as a product of singlet fission is well established in the literature, and control of quintet formation is an important step towards applying singlet fission in photovoltaics and quantum information. However, a definitive mechanism for quintet formation is yet to be established, which makes it difficult to design materials for optimal quintet formation. Here we outline a mechanism in which inter-triplet exchange-coupling fluctuations drive fast and efficient quintet formation. We show that quintet formation is possible even in the strong-exchange regime, in accordance with recent experimental prediction. We evaluate the performance of this quintet formation mechanism in two regimes of conformational freedom, and relate quintet dynamics to material properties of singlet fission molecules.

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Exchange interactions between electrons with overlapping wavefunctions arise from exchange symmetry. Engineered exchange interactions underpin many new technologies, including spintronics, quantum information, magnetic materials, and spin-dependent chemical processes. In many of these applications, precise control of the exchange interaction is also critical. However, as with all realistic systems, these exchange interactions are subject to noise.

Exchange noise can arise from many sources (Fig. 1a), including thermally-driven structural fluctuations, switching in nearby charge centres[1,2], and electrical noise in voltages applied to control gates[3,4] in engineered systems. Quantum dot systems[5,6] are a prime example of this, and due to their potential applications in quantum information processing, advanced approaches to quantifying the impact of exchange noise have been developed[7]. Fundamentally, these approaches have sought to efficiently model open quantum systems (OQS), i.e., quantum systems coupled to their environment[8], as a way to understand and improve the fidelity of gate operations[9,10]. Interestingly, there are systems where exchange noise, instead of being a detriment, plays a necessary part in useful quantum processes[11,12]. In this work, we apply OQS modelling techniques to understand how the fluctuation of exchange coupling produces high-spin states in singlet fission.

Singlet fission is a photophysical process that occurs in molecular systems, wherein an optically prepared singlet (spin-0) exciton forms a pair of triplet (spin-1) excitons on neighbouring chromophores[13]. The process has been the subject of fundamental spectroscopic studies since the 1960s[14,15] and has received renewed interest this century due to its potential use in photovoltaic devices[16–19] and medical imaging[20]. Since singlet fission proceeds rapidly from a singlet state, it is assumed to form the net-singlet triplet-pair ^{1}(TT), i.e., a pair of triplets whose spins couple with zero net spin. However, recent spectroscopic studies have revealed that the triplet-pair undergoes spin dynamics, forming triplet ^{3}(TT) and quintet ^{5}(TT) multiexcitons[21,22], before dissociating into uncorrelated triplet excitons. High-spin states such as quintets have fundamental implications for the use of singlet fission in photovoltaics[22] and have also been considered for quantum information processing applications[23]; understanding how these high-spin states form in singlet fission and how material design can affect their formation presents an important unanswered question in the field[23].

One proposed mechanism for high-spin state generation is the fluctuation of the inter-triplet exchange coupling[24,25]. Given that the exchange coupling strength is sensitive to inter-triplet wavefunction overlap, such fluctuations likely arise from the nuclear motions of the molecules hosting the excitons[26]. In a recent work[24], the authors show that transitions from weak to strong exchange, mediated by conformational motion, offer a pathway for quintet formation. However, such a mechanism predicts quintet formation to occur in nanoseconds, disagreeing with the microsecond rise time seen experimentally[21].

Meanwhile, experimental evidence suggests that quintet formation may be driven by conformational dynamics even if nuclear reorganisation proceeds within picosecond timescales[26]. Furthermore, the broadness of EPR (electron paramagnetic resonance) spectra, directly linked to the strength of the exchange interaction, provides an additional indication that quintets might form even in the strong exchange regime[21]. Indeed, no magnetic resonance studies of covalent singlet fission dimers to date demonstrate the formation of weakly coupled high-spin states prior to strongly-coupled high-spin states. All these observations urge clarification and lead us to two essential questions: Can quintet multiexciton formation proceed efficiently even in the strong-exchange regime? And if so, what are the ideal conformational properties—e.g., looseness or stiffness of the host molecule—for enhancing or inhibiting spin-mixing?

In this work, we systematically address these questions using an open quantum system approach to model the dynamics of the correlated triplet pair (TT) as it interacts with its environment. By considering the paradigmatic cases of stochastic conformational switching—inspired by recent experimental work[26]—and harmonic conformational motion, we show that quintet formation can proceed efficiently even if the exchange interaction is orders of magnitude larger than the coupling between singlets and quintets. With exact numerical solutions and fundamental results from the theory of open quantum systems, we precisely interpret the mechanisms by which conformational dynamics assist high-

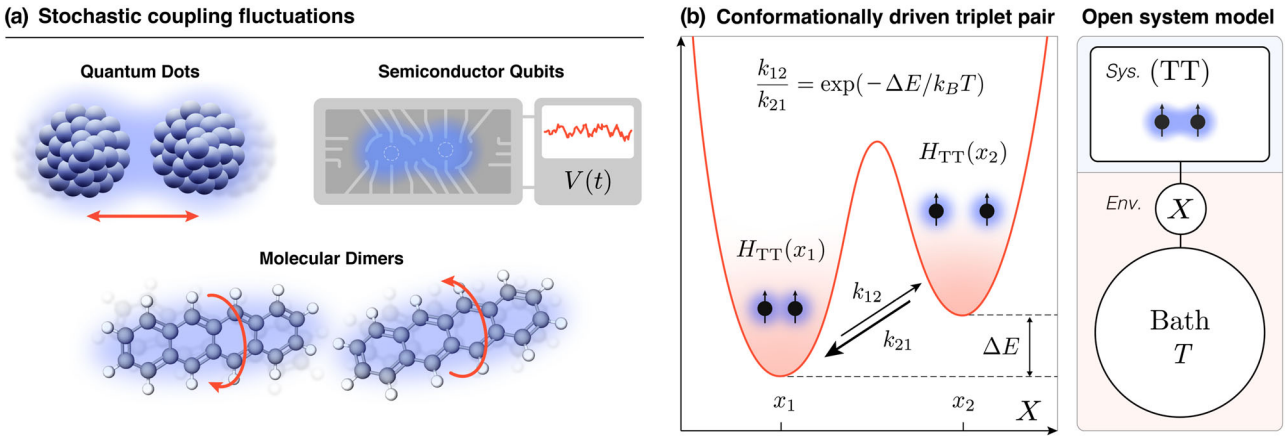

Fig. 1 Outline of the noisy-exchange model. a Exchange coupling fluctuations that arise from various sources of noise are ubiquitous. They often negatively affect the performance of quantum information processing of quantum dots and superconducting qubits[4]. In molecular dimers, exchange coupling fluctuations can instead be beneficial, as we show in this work, for the formation of high-spin states. **b** We consider a system given by a triplet pair (TT), consisting of two spin-1 particles, that undergoes spin mixing due to fluctuations in the spin Hamiltonian $H_{TT}(x_t)$ driven by a conformational coordinate X. The latter interacts with a large bath of nuclear vibrations at thermal equilibrium with temperature T. In the Results, we focus on the case of exchange fluctuations $J(x_t)$ and discuss how the efficiency of quintet formation depends on the stochastic process $\{X(t) : t \in \mathbb{R}_+\} \mapsto \{J(x_t)\}$, whose two-time correlation functions respect the thermodynamic detailed balance condition. For example, if the conformational coordinate has only two states, all dynamics are described by the forward and reverse transition rates k_{12}, k_{21} whose ratio is determined by the difference in energy ΔE of the conformations, Boltzmann's constant k_B, and the system temperature T.

spin state formation. We also present closed-form expressions for the optimal conditions for quintet formation, and calculate the dependence of quintet formation on temperature, magnetic field, and the noise power spectrum of the conformational dynamics. We conclude by discussing the significance of our results from both fundamental and practical standpoints.

Results

Methods. The system considered in this work is the correlated triplet pair (TT), modelled using the spin Hamiltonian

$$H_{\mathrm{TT}} = H_{\mathrm{z}} + H_{\mathrm{zfs}} + H_{\mathrm{ee}}, \tag{1}$$

given by the sum of Zeeman (z), zero-field splitting (zfs) and exchange (ee) interactions[27], as done previously[21,24,26]. We ignore the effects of triplet diffusion by assuming the pair to sit on two neighbouring sites of a dilute crystal or on a molecular dimer[21,26,28–30]. To focus on the strong-exchange regime, we set the exchange strength to be much larger than the zero-field splitting and Zeeman interactions, i.e., $\|H_{\mathrm{zfs}}\|/\|H_{\mathrm{ee}}\|, \|H_{\mathrm{z}}\|/\|H_{\mathrm{ee}}\| \ll 1$, by the account of the spectral norm $\|\cdot\|$. Explicit expressions for the terms in the Hamiltonian of Eq. (1) are given in Supplementary Note 1.

The singlet, triplet, and quintet states (denoted ^{1}(TT), ^{3}(TT), and ^{5}(TT), respectively) are defined as eigenstates of the total-spin operator S^2 of the triplet pair. Since both H_z and H_{ee} commute with S^2, they cannot mix ^{1}(TT) with the high-spin states, while H_{zfs} can. In the Results, we fix the parameters of H_{zfs} such that the two triplet excitons are indistinguishable, preventing ^{1}(TT) (symmetric under permutation of triplets) from mixing with ^{3}(TT) (antisymmetric). As we will discuss in Stochastic conformational switching at zero-field, this choice remarkably simplifies the rationalisation of the spin dynamics, which can often be reduced to that of a two-level system. Nevertheless, our approach is of general validity and can be applied to arbitrary choices of zero-field splitting parameters.

To study the role of conformational motion on multiexciton dynamics, we consider the simplified scenario in which a single conformational coordinate X is responsible for the fluctuations of the exchange interaction strength $J(x_t)$[27], with x_t being the value of X at time t. Note that the coordinate X is not necessarily a proxy for the physical distance between two sites and could, for example, represent the asymmetry parameter of a double quantum well or the dihedral angle between two planar molecules. In the Results, we assume for simplicity that the H_{zfs} parameters do not vary with x_t; this can be justified by proposing that the rotation of a phenyl bridge in an acene dimer[31] will only affect the exchange coupling and not the H_{zfs} parameters. We discuss fluctuating H_{zfs} in Supplementary Note 5. A large ensemble of nuclear vibrations, here modelled as a phonon bath at thermal equilibrium, is directly coupled only to X (as shown in the schematic of Fig. 1b), driving transitions between different conformational configurations.

Throughout this work, we assume that the dynamics of the conformational coordinate X and that of the bath are not affected by that of the triplet pair, as often done in the literature[26,32]. This allows us to study the dynamics of (TT) in two regimes of conformational dynamics: stochastic switching and perturbed harmonic oscillations.

First, we consider the case in which the vibrational bath drives stochastic switching of X between two configurations x_1 and x_2, as depicted in Fig. 1. This is akin to the systems considered by Kobori et al.[26] and by Korovina et al.[33]. This model is physically well motivated for stable and thermally accessible configurations x_1, x_2 (e.g., asymmetric double-well potentials), energetically separated by $\Delta E \coloneqq E(x_2) - E(x_1) > 0$ (without loss of generality) such that the thermal energy $k_B T$ at temperature T is sufficiently large to induce hopping between the local equilibria[34]. In Stochastic conformational switching at zero-field, we use this model to study quintet formation in the strong-exchange regime at zero-field, i.e., in the absence of Zeeman interaction. The effects of magnetic field intensity and orientation are discussed in Magnetic field effects on stochastic conformational switching.

We then consider a continuous conformational space in Harmonic conformational dynamics at zero-field, where we model X as a harmonic mode with characteristic frequency ω. The mode exchanges energy with the thermal bath at some rate $\Gamma^{(X)}(\Delta E, T)$ that respects the thermodynamic detailed balance condition. With this model, we aim to study high-spin state formation driven by a conformational coordinate that oscillates around a unique thermally-accessible local equilibrium. By studying the dynamics of (TT) over the parameter space spanned by ω and $\Gamma_0^{(X)} = \Gamma^{(X)}(0, T)$, we highlight the relation between quintet formation efficiency and the noise power spectrum (i.e., noise colour) of the conformational stochastic process $\{X(t) : t \in \mathbb{R}_+\}$[35]. The role of the noise memory kernel is then framed in terms of Markovian and non-Markovian[36,37] conformational driving of the spin manifold.

Stochastic conformational switching at zero-field. Let us consider the system of Eq. (1) in the absence of an external magnetic field $\boldsymbol{B}$ ($H_z = 0$). The stochastic switching of X affects the strength $J(x_t)$ of the exchange interaction, which takes the value J_i at configuration x_i. The conformational dynamics are fully described by the rates k_{ij} of switching from configuration x_i to x_j. Note that the rates k_{ij} do not depend on the (TT) states because the spin dynamics are assumed to not affect that of X.

To study the dynamics of the correlated triplet pair, we consider the Hilbert space $\mathcal{H} = \mathcal{H}_{\mathrm{TT},x_1} \oplus \mathcal{H}_{\mathrm{TT},x_2}$ associated with the system (TT) at configurations x_1 and x_2, and rearrange it as $\mathcal{H} = \mathcal{H}_X \otimes \mathcal{H}_{\mathrm{TT}}$. The dynamics of the state density matrix ρ_t is then determined by the following Lindblad master equation

$$\dot{\rho}_t = \frac{\mathrm{i}}{\hbar}[\rho_t, H] + \sum_{\substack{i=1,2\\ j\neq i}} k_{ij}\left(L_{ij}\rho_t L_{ij}^\dagger - \frac{1}{2}\left\{L_{ij}^\dagger L_{ij}, \rho_t\right\}\right), \tag{2}$$

where $\dagger$ denotes the Hermitian conjugate and $\{\cdot,\cdot\}$ is the anticommutator. Here, $H = \sum_{i=1,2}\Pi_{x_i} \otimes H_{\mathrm{TT}}(x_i)$, where $\Pi_{x_i} = |x_i\rangle\langle x_i|$ is the projector on configuration x_i, and $H_{\mathrm{TT}}(x_i)$ is the Hamiltonian of Eq. (1) at configuration x_i. Similarly, the Lindblad (jump) operators $L_{ij} = |x_j\rangle\langle x_i| \otimes \mathbb{1}_{\mathrm{TT}}$ model stochastic conformational switching $x_i \to x_j$ at rate k_{ij}, without acting on the state of the correlated triplet pair. Eq. (2) provides a Markovian description of the (TT) dynamics averaged over the ensemble of all possible conformational trajectories. Note that this approach is non-perturbative in $H_{\mathrm{TT}}(x_i)$, so we can consider arbitrary dependence of the spin Hamiltonian on X.

Eq. (2) is solved using the Liouville superoperator approach $\dot{\boldsymbol{\rho}}_t = \mathcal{L}\boldsymbol{\rho}_t$ to obtain $\boldsymbol{\rho}_t = \exp[\mathcal{L}t]\boldsymbol{\rho}_0$, where $\mathcal{L}$ is the Liouville superoperator associated with Eq. (2), and where the initial state $\rho_0 = |x_2\rangle\langle x_2| \otimes |^1(\mathrm{TT})\rangle\langle ^1(\mathrm{TT})|$ is assumed to be the singlet state ^{1}(TT) at the high-energy configuration x_2. This choice reflects the intention of studying singlet fission as a non-equilibrium process that, following photoexcitation, proceeds via thermal relaxation starting from an out-of-equilibrium state of (TT) and X[32].

Our results, presented in Fig. 2 for a particular choice of zero-field splitting and exchange parameters (see Supplementary Note 1), show the average population $p_5(t)$ of the quintet manifold

$$p_5(t) = \sum_{m=-2}^{2} \mathrm{Tr}[\rho_t\, \mathbb{1}_X \otimes |\,^5(\mathrm{TT})_m\rangle\langle\, ^5(\mathrm{TT})_m|], \tag{3}$$

where $^5(\mathrm{TT})_m$ is the quintet state with spin projection m as a function of the switching rates k_{ij}. From our solution, it is evident

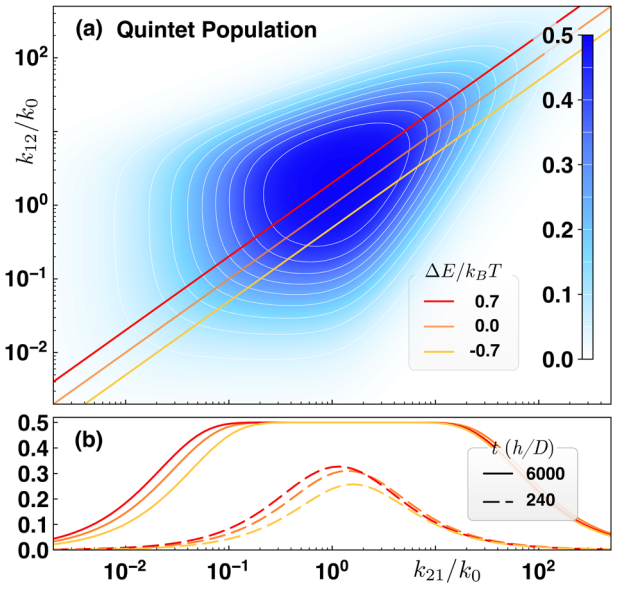

Fig. 2 Quintet formation driven by stochastic conformational switching at zero-field. a Blue shading indicates quintet population $p_5(t)$ for $t = 1200$ periods (one period is h/D, Planck's constant divided by the ZFS constant D) or ≈ 1.05 μs, as a function of the switching rates k_{12}, k_{21} in units of $k_0 = 3(J_1 + J_2)/2h$. This is in accordance with the μs rise time of quintets measured by Tayebjee et al.[21]. Quintet formation proceeds efficiently when the stochastic resonance condition of Eq. (5) is respected. Warm-coloured lines indicate regions of constant $k_{21}/k_{12} = \Delta E/k_BT$ where ΔE is the energy difference between the two conformations, k_B is Boltzmann's constant, and T is the temperature. **b** Slices of $p_5(t)$ at different k_{21}/k_{12} values for two different times. The stochastic resonance condition for rates is not generally symmetric in k_{ij}. Stochastic resonance drives quintet formation by switching between two non-commuting spin Hamiltonians. At the individual trajectory level, ^{1}(TT) and ^{5}(TT) can undergo complete population inversion. However, the ensemble average of $p_5(t)$ never exceeds 1/2. This is because, for sufficiently long times, each individual spin trajectory ergodically explores the space of accessible states, driving the ensemble towards the state of maximal entropy. See Supplementary Note 1 for parameters of the spin Hamiltonian.

that quintet formation can proceed efficiently—i.e., with significant quintet/singlet population ratios—and rapidly—i.e., within the ns to μs timescale characteristic of high-spin lifetimes in EPR experiments[38]—even in the strong-exchange regime. For example, Fig. 2a shows that certain switching rates bring about a 50/50 equilibrium between singlet and quintet populations within 1.05 μs of singlet fission. Hence our results provide a prescription for the optimisation of the conformational switching parameters k_{ij} for enhancing quintet formation.

The mechanism of spin-mixing presented in Fig. 2 can be rationalised by representing the correlated triplet pair in terms of an equivalent two-level system (TLS). In the absence of a magnetic field and assuming parallel chromophores, the initial singlet state $|^1(\mathrm{TT})\rangle$ only couples with one state, a quintet, here denoted by $|^5(\mathrm{TT})\rangle$ for brevity. Under these conditions, the spin Hamiltonian can be rewritten as

$$H_{\mathrm{TLS}} = -\frac{\Delta}{2}\sigma_x - \frac{\varepsilon(x_t)}{2}\sigma_z, \tag{4}$$

where σ_x and σ_z are Pauli operators. Here $\Delta = -2\langle^1(\mathrm{TT})|H_{\mathrm{TT}}|^5(\mathrm{TT})\rangle$ is directly associated with the zero-field splitting parameters coupling $|^1(\mathrm{TT})\rangle$ and $|^5(\mathrm{TT})\rangle$, while $\varepsilon(x_t) = \langle^5(\mathrm{TT})|H_{\mathrm{TT}}|^5(\mathrm{TT})\rangle - \langle^1(\mathrm{TT})|H_{\mathrm{TT}}|^1(\mathrm{TT})\rangle$ is related to the strength $J(x_t)$ of the exchange interaction and the zero-field splitting parameters; see Supplementary Note 2 for the explicit expressions of Δ and ε.

The spin dynamics can now be represented on the Bloch sphere[39]: An initial singlet state $|^1(\mathrm{TT})\rangle \leftrightarrow -\hat{\boldsymbol{z}}$ precesses around the axes $\boldsymbol{h}_i = \Delta\hat{\boldsymbol{x}} + \varepsilon(x_i)\hat{\boldsymbol{z}}$ at frequency $\omega_i = \| \boldsymbol{h}_i \| /\hbar = \sqrt{\Delta^2 + \varepsilon(x_i)^2}/\hbar$. In the strong-exchange regime $\Delta \ll \varepsilon(x_t)$, the quickest way to reach the quintet state $|^5(\mathrm{TT})\rangle \leftrightarrow \hat{\boldsymbol{z}}$ is to switch between conformations $x_i \to x_j$ after time intervals $\tau_{ij} \simeq \pi/\omega_i$, i.e., in resonance with each conformation's precession frequency. Supplementary Note 3 contains a detailed discussion of this geometric argument.

In the case of stochastic conformational switching (here, with exponential distribution), quintet formation is enhanced when the switching rates k_{ij} match the precession frequencies so that the average switching time $\langle\tau_{ij}\rangle \approx \pi/\omega_i$. This relation, well-known as the statistical synchronisation condition (Stochastic resonance occurs when the average switching time matches half the period of periodic driving[34]), allows us to pinpoint stochastic resonance[34,40] as the fundamental mechanism responsible for efficient quintet formation in the strong-exchange regime. The ideal conditions for enhancing quintet formation are, therefore, to be sought using

$$k_{ij} = \frac{\sqrt{9J_i^2 - 4J_iD + 4D^2}}{\hbar\pi}, \tag{5}$$

where Δ and ε have been expressed in terms of $J_i = J(x_i)$ and D, the relevant exchange and zero-field splitting parameters (See Eqs. (S9), (S10) in Supplementary Note 2.) In the limit of strong exchange $J(x_t) \gg D$ the condition reduces to $k_{ij} = 3J_i/\hbar\pi$.

This observation has two major implications: First, it points at the opportunity of exploiting conformational dynamics with peaked stochastic switching distribution (e.g., Poisson statistics) to further refine the resonance condition, even in the Markovian limit. This can enhance the quintet formation rate, as we discuss in Harmonic conformational dynamics at zero-field.

Second, it opens the doors towards the coherent preparation of high-spin states by means of controlled switching of the exchange interaction strength. This may be achieved by applying an electric field to modulate the overlap of the electronic wave functions[41] or by means of conformational switching. Optically controlled conformational switching, or photoswitching, is a pioneering approach to control the chemical and optical properties of molecular materials[42–44]. Since photoswitching is in itself a stochastic process, the feasibility of photoswitching-assisted high-spin preparation depends on our ability to match the switching rates to the spin-mixing resonance conditions, requiring further refinement of dynamical modelling. In Supplementary Note 3, we present an elementary protocol for a switching sequence that can be used to prepare a specific quintet state. We anticipate this approach to receive significant attention for its potential applications.

Before looking at the influence of the magnetic field on the spin-mixing dynamics, let us discuss how our results can be used to guide the design of singlet fission materials[31]. Imposing the detailed balance condition on the conformational switching rates $k_{ij}/k_{ji} = \exp[-\Delta E/k_BT]$ provides a proxy for the temperature dependence of the quintet formation rate, as illustrated in Fig. 2b. We can now interpret our results in terms of stiffness and looseness of the conformational coordinate: When the energetic separation ΔE between the stable configurations x_1 and x_2 is much larger than the thermal energy of the bath (i.e., X is stiff), quintet formation is inhibited. The same outcome is expected for sufficiently low temperatures T, such that the coordinate X is considered to be frozen. This is consistent with the experimental findings by Kobori et al.[26], where a fast-oscillating conformational switching (with frequency in the THz range) is identified

as responsible, over other slower modes, for quintet formation following singlet fission in TIPS-pentacene molecular dimers. Note that spin-mixing is also inhibited when both rates are too slow, too fast, or generally away from the stochastic resonance condition.

Magnetic field effects on stochastic conformational switching. Magnetic field experiments are crucial for identifying the effects of spin on organic electronic processes such as singlet fission. The assumption of no field in Sec 3A simplifies the calculation but prevents comparison between this theory and the various spin-probing experiments such as EPR and ODMR (optically detected magnetic resonance.) In this section, we explore how a static magnetic field $\boldsymbol{B}$, with variable magnitude $B = |\boldsymbol{B}|$ and orientation relative to the molecule $\hat{e}_B = \boldsymbol{B}/B$, affects quintet formation in the stochastic switching model of the previous section.

Note that the field parameters here are simplified by two assumptions: our dimers are coplanar, and so share a common z-axis, $\hat{\boldsymbol{z}}_{\rm M}$; and the ZFS parameter E is set to zero (details are in Table S1, Supplementary Note 1.) Hence our molecule spin Hamiltonian has $D_{\infty \rm h}$ symmetry (i.e it is invariant under rotations about $\hat{\boldsymbol{z}}_{\rm M}$), so the field direction $\hat{\boldsymbol{e}}_B$ is uniquely determined by the angle θ between $\hat{\boldsymbol{e}}_B$ and $\hat{\boldsymbol{z}}_{\rm M}$.

Changing the field orientation changes the symmetry of the spin Hamiltonian $H_{\rm TT}$, which affects the number of ^{5}(TT) states that are accessible from ^{1}(TT)[30]. In Fig. 2, when only one ^{5}(TT) state can be accessed from ^{1}(TT), the ^{5}(TT) population saturates at 50%. If ^{1}(TT) were able to mix with more of the ^{5}(TT) states, two things should occur: The ^{5}(TT) population should saturate at higher percentages, and the net rate of the ^{5}(TT) population should increase, as ^{5}(TT) formation becomes entropically favourable. These magnetic field effects are qualitatively similar to those studied by Merrifield et al.[45] to explain the effects of magnetic field on triplet exciton dynamics.

Figure 3 shows the quintet population at $t = 2000h/D \approx 1.76\,\mu$s, which is a sufficiently long time for the quintet population to nearly saturate for every value of the field parameters. Figure 3a shows how the quintet population varies with θ and B. Both extremes of $H_{\rm TT}$ symmetry can be seen: there are regions where only one ^{5}(TT) state mixes with ^{1}(TT), so the quintet population saturates at 0.5, and regions where all five ^{5}(TT) states mix and quintet population saturate at $5/6 \approx 0.83$. While the two-conformation stochastic model is simple, it allows us to draw qualitative conclusions about how the quintet formation rate varies with field direction. This information may be fruitfully coupled with EPR and ODMR experiments, which are able to detect quintet populations in a way that is sensitive to field direction[46]. For example, at a high field, the region of the EPR/ODMR spectrum corresponding to $\theta = 50°$ is predicted here to form quintets more slowly than, say, $\theta = 70°$.

Figure 3b shows the quintet population as a function of B for $\theta = 4°$, $\theta = 10°$, and averaged over all θ values. There are two pronounced peaks when θ is small, coinciding with level crossings of the ^{5}(TT) sublevels, as shown in Fig. 3d. These level crossings are plotted for $\theta = 0$, in which case the crossings are not avoided, but small variations in θ cause the crossings to become avoided while only slightly changing where the crossings occur. While these crossings occur far below conventional EPR fields, they may be visible in magneto-photoluminescence experiments, which can indirectly observe ^{5}(TT) formation as a lack of ^{1}(TT) absorption signal.

Lastly, Fig. 3c shows quintet population varying with B while θ is held constant. It is clear that when $\theta = 0$, i.e $\boldsymbol{B}$ is aligned with the molecular z-axis $\hat{\boldsymbol{z}}_{\rm M}$, only one ^{5}(TT) state can mix with ^{1}(TT). $\theta = 90°$ also shows less than the maximal quintet yield, with

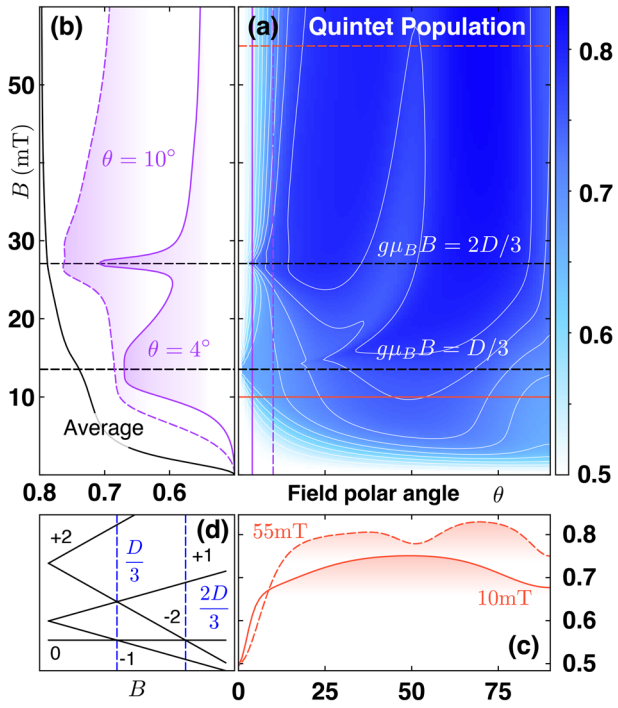

Fig. 3 Effect of magnetic field on quintet formation driven by stochastic conformational switching. a Quintet population $p_5(t)$ at $t = 2000h/D \approx 1.76\,\mu$s ($h$ Planck's constant, D the ZFS parameter) as a function of the field polar angle θ and the magnetic field strength B. g is the electron g-factor and μ_B the Bohr magneton. **b** Slices of $p_5(t)$ for fixed angles as a function of B, with the weighted average of p_5 over all angles in black. The peaks in the $\theta = 4°$ slice correspond to the level crossings shown in panel (**d**). **c** Slices of $p_5(t)$ for fixed field strength as a function of θ. The dips at $\theta = 0°$, 54. 7°, and 90° occur where some ^{5}(TT) eigenstates cannot mix with ^{1}(TT)[30]. **d** Quintet energy levels vary with magnetic field strength, with field direction $\hat{\boldsymbol{e}}_B$ parallel to the molecular z-axis $\hat{\boldsymbol{z}}_{\rm M}$. Any deviation in $\hat{\boldsymbol{e}}_B$ causes the crossings to become avoided, allowing more than one ^{5}(TT) state to mix with ^{1}(TT). See Supplementary Note 1 for parameters of the spin Hamiltonian.

^{5}(TT) populations saturating at 3/4, since only three ^{5}(TT) states mix with ^{1}(TT) as predicted by Smyser et al.[30].

The results of this section show that even if the magnetic field is weak compared to exchange coupling ($\|H_{\rm z}\|/|H_{\rm ee}\| \approx 0.01$), it can greatly affect the rate of quintet formation in the stochastic switching model. Firstly, this suggests magnetic field as a valuable control parameter for quintet generation, supplementing the conformational properties proposed in the previous section. Secondly, it allows for the results of already common experimental measurements of quintet formation, such as EPR and ODMR spectroscopy, to be interpreted without assuming weak exchange coupling[21].

Harmonic conformational dynamics at zero-field. We now generalise our results to the case of a continuous conformational space by modelling X as a harmonic mode coupled to a thermal bath. For the sake of clarity, we go back to the spin Hamiltonian considered in Stochastic conformational switching at zero-field by setting $H_{\rm z} = 0$. This choice simplifies the solution of the spin dynamics and the interpretation of the results by reducing the triplet-pair to the equivalent TLS of Eq. (4).

The conformational coordinate X, whose dynamics is still independent of the state of the spins, is here modelled as a harmonic oscillator with characteristic frequency ω, which exchanges

energy ΔE with the bath at temperature T at rate $\Gamma^{(X)}(\Delta E, T)$ such that $\Gamma^{(X)}(0, T) = \Gamma_0^{(X)}$, here referred to as the *oscillator dephasing rate*. The trajectories x_t of X correspond to harmonic oscillation $A\cos(\omega t + \phi)$ around an equilibrium $x_0 = 0$ (without loss of generality), intermitted by stochastic changes of phase and amplitude $(A, \phi) \to (A', \phi')$; these are sampled numerically as described in Supplementary Note 4.

Dealing with a continuous conformational space, we now study the spin dynamics using the time-dependent Schrödinger equation $i\hbar d_t|\psi_t\rangle = H_{\mathrm{TT}}(t)|\psi_t\rangle$, where the Hamiltonian $H_{\mathrm{TT}}(t)$ depends on conformational trajectories via $J(x_t)$—here, a linear function of x_t—and where $|\psi_t\rangle$ is the state of the correlated triplet pair time t. The solution $|\psi_t\rangle = U(t, t_0)|\psi_0\rangle$ along a trajectory x_t can be expressed in terms of the Dyson series $U(t, t_0) = \mathcal{T}\{\exp[-i\int_{t_0}^{t} ds H_{\mathrm{TT}}(s)]\}$[36]. The spin dynamics ρ_t of the ensemble is then obtained by averaging over a large number of trajectories, as discussed in Supplementary Note 4.

As done in the previous sections, we focus on the average population of the quintet manifold $p_5(t)$, here calculated by dropping the $\mathbb{1}_X$ term from Eq. (3). In Fig. 4a, we show how $p_5(t)$ depends on the conformational frequency ω and on the oscillator dephasing rate $\Gamma_0^{(X)}$, by fixing the temperature of the bath T. As anticipated in Stochastic conformational switching at zero-field, relaxing the condition of purely stochastic conformational dynamics ($x_i \to x_j$ at rate k_{ij}), we allow for non-trivial correlation timescales for the conformational trajectories, $\langle x_{t'} x_t\rangle \not\propto \delta(t' - t)$, thus opening up to the possibility of partially coherent resonant driving of the correlated triplet pair. This leads to enhanced resonance conditions that can outperform the quintet formation efficiencies typical of stochastic resonance.

The fundamental difference from the stochastic switching of the previous sections is highlighted by the formation of the resonance regions for $\Gamma_0^{(X)} \ll \omega$ shown in Fig. 4. The peak of the resonance fringes can be found at $\omega_k = \varepsilon(x_0)/k$ (cf. Eq. (4)) for positive natural numbers k, as prescribed by the diabatic limit of the Landau–Zener–Stückelberg theory of periodically driven two-level systems[47]. Larger resonance frequencies ω_k induce faster mixing and, therefore, higher peaks (see Fig. 4b, c) due to the higher number of LZS passages[47]. Note that the LZS theory, based on the Hamiltonian of Eq. (4) for the case of harmonic oscillations of $\varepsilon(t) = \varepsilon_0 + A\sin(\omega t)$, provides closed-form solutions only for the resonance conditions in the slow-driving (adiabatic) and fast-driving (diabatic) regimes, given by $A\omega \ll \Delta^2$ and $A\omega \gg \Delta^2$, respectively. Our exact numerical solutions complement the theory while demonstrating the robustness of the resonance conditions outside the limit cases.

Once again, these results have significant implications for the design of singlet fission materials, as the formation of high-spin states can be tuned by means of resonant (or off-resonant) conformational motion. The detailed balance condition $\Gamma^{(X)}(\Delta E, T)/\Gamma^{(X)}(-\Delta E, T) = \exp[\Delta E/k_B T]$ can be used to determine the ideal stiffness or looseness of the conformational environment to achieve the desired spin-mixing, suggesting that resonance fringes would be more evident at low temperatures for X weakly coupled to the thermal bath.

Finally, we would like to remark on how the noise power spectrum $S_J(\omega) = \mathcal{F}[c_J(t + \tau, t)]$ of the stochastic process associated with the time variation of exchange strength $J(t)$, given by the Fourier transform of its autocorrelation function $c_J(t + \tau, t) = \langle J(t + \tau)J(t)\rangle$, provides sufficient information to determine if, and how well, the resonance conditions are met. It further highlights the difference between stochastic resonance, which occurs for purely Markovian processes characterised by trivially correlated white noise, and the stronger, partially coherent resonance that arises for processes with coloured noise power spectrum profiles.

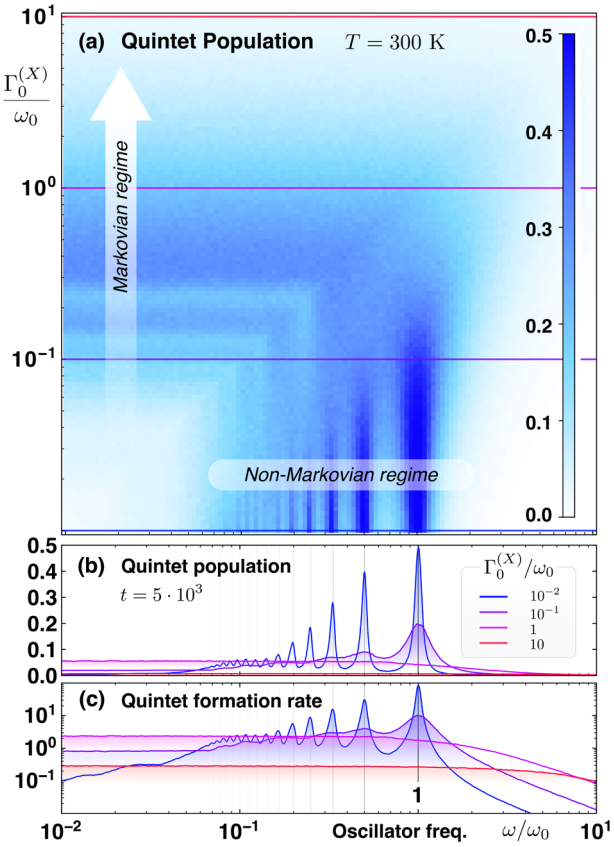

Fig. 4 Quintet formation driven by harmonic conformational dynamics. **a** Quintet population for $t = 5000$ periods ($\hbar/\varepsilon_0$), at $T = 300$ K, as a function of the oscillator frequency ω and oscillator dephasing rate $\Gamma_0^{(X)}$ (frequencies and rates expressed in units of $\omega_0 = \varepsilon_0/\hbar$, 1000 trajectories for each point). Here $\hbar$ is the reduced Planck constant, and ε_0 is defined in Supplementary Note 2. We depict quintet population (**b**) and quintet formation rate (**c**) along slices of constant $\Gamma_0^{(X)}$ (see the legend.) Quintet formation rate γ is extracted from population data as a fit to $p_5(t) = [1 - \exp(-\gamma t)]/2$. Pronounced resonance peaks can be seen for $\Gamma_0^{(X)} \ll \omega$ (non-Markovian regime) at $\omega = \varepsilon_0/\hbar k$, with k positive natural numbers. Their positions are prescribed by the diabatic limit ($\omega \gg \Delta^2/A$) of multiple-passage Landau–Zener–Stückelberg theory (LZS)[47]. Increasing $\Gamma_0^{(X)}$ decreases the coherence of the oscillator, so there is less opportunity for the Stückelberg phase of the triplet pair to accumulate over several periods of oscillation. This results in the resonance peaks broadening to the point of indistinguishability for moderate $\Gamma_0^{(X)} \gg \omega$ (Markovian regime). See Supplementary Note 1 for parameters of the spin Hamiltonian.

Conclusions

In this letter, we have shown how high-spin states can be generated efficiently in singlet fission, even in the strong-exchange regime, when driven by favourable conformational dynamics. This spin-mixing mechanism, here solved for the paradigmatic cases of stochastic switching and harmonic oscillations, is fundamentally different from the one described previously[24], where quintet formation proceeds in the nanosecond timescale via conformational reorganisations that briefly suppress the exchange interaction. In practice, we expect these two mechanisms to coexist and to be experimentally discernible via the different lifetimes and coherence timescales of the generated quintets.

The stochastic and coherent resonance conditions derived in the Results are key for the engineering of singlet fission materials. They can be used as guidelines to enhance or inhibit the formation of high-spin states, depending on whether they are beneficial or detrimental for tasks like exciton transport and spin-

mediated spectral conversion. Our findings also open the path to spin-selective state preparation by coherently switching the exchange interaction strength, which may be controlled with electric fields[41] or via conformational photoswitching[44]. This can impact quantum information processing architectures[30,48] and help in the experimental interrogation of the fundamental physics of high-spin states, such as their lifetime and interactions with the bath of nuclear spins[49].

The considered open quantum system formulation of singlet fission, similar to that used in previous works[13,32,50], is a powerful tool for the quantitative study of spin-mixing in singlet fission for specific materials and can be generalised to account for spin-orbit coupling, spin migration, and other phenomena. It also provides the natural mathematical framework to implement coherent control tasks like fiducial state preparation, which can be tackled using quantum optimal control protocols[51–53], and, possibly, saturate bounds for time-optimal state preparation[12,54]. By ignoring the effects of triplet diffusion, our results hold for the case of molecular dimers arrangements and dilute crystalline materials with sufficiently low triplet exciton mobility[30]. More complex materials like 2D and 3D spin lattices with higher triplet mobility can instead be efficiently addressed using an analogue formulation based on density matrix renormalisation group and tensor network methods[55,56].

Data availability

All data were generated for this manuscript, with no reference to pre-existing datasets. All data and code are available upon request.

Code availability

The datasets, and the scripts used for their generation, are available upon request.

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Author contributions

The study was conceived by D.R.M. and J.H.C. Different models was developed by M.I.C., F.C., and J.H.C. with input from D.R.M. and M.J.Y.T. on their physical validity. Simulations were performed by M.I.C. and F.C. All authors contributed to the discussion and analysis of the results. The manuscript was written by M.I.C. and F.C. with contributions from all authors.

Competing interests

All authors declare no competing interests.

Additional information

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