Multi-exciton generation in molecular semiconductors via singlet fission

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1 Singlet fission Hamiltonian

The singlet fission Hamiltonian[1] H_{ex} is composed of singlet (H_S), triplet (H_T), and singlet-triplet interaction terms (H_{int}),

$$H_{\text{ex}} = H_S + H_T + H_{\text{int}}. \tag{1}$$

We will consider 1D rings of identical molecules, with identical optical dipoles moments all oriented along the same direction. This system is modelled as a one-dimensional periodic lattice with nearest-neighbour couplings. We will use the following local exciton basis,

$$\mathcal{B}_i := \{|S_0\rangle_i, |S_1\rangle_i, |T_1\rangle_i\}, \quad i = 1, \ldots, N, \tag{2}$$

consisting of the ground singlet exciton $|S_0\rangle_i$, the first excited singlet exciton $|S_1\rangle_i$, and the triplet exciton $|T_1\rangle$.[2] This means that the local Hilbert space dimension of the exciton is $d_{\text{ex}} = 3$. Feel free to choose any other notation for the basis states, e.g., $\mathcal{B}_i = \{|0\rangle_i, |1\rangle_i, |2\rangle_i\}$.

1.1 Singlet term

Le $\mathcal{S}_i^\dagger$ be the singlet creation operator associated with the transition $|S_0\rangle_i \to |S_1\rangle_i$ between the local ground state (S_0) and singlet excited state (S_1) at site i. The singlet Hamiltonian is,

$$H_S = \sum_{i=1}^N \varepsilon_S \mathcal{S}_i^\dagger S_i + \sum_{i=1}^N \left(J_S \mathcal{S}_i^\dagger \mathcal{S}_{i+1} + h.c. \right), \tag{3}$$

with periodic boundary conditions, where ε_S is the energy of a singlet with respect to the ground state, and J_T is the hopping strength of the singlets.

1.2 Triplet term

Let $\mathcal{T}_i^\dagger$ be the triplet creation operator associated with the transition $|S_0\rangle_i \to |T_1\rangle_i$. Then, the triplet Hamiltonian is,

$$H_T = \sum_{i=1}^N \varepsilon_T \mathcal{T}_i^\dagger \mathcal{T}_i + \sum_{i=1}^N \left(J_T \mathcal{T}_i^\dagger \mathcal{T}_{i+1} + h.c. \right) + \sum_{i=1}^N \chi \mathcal{T}_i^\dagger \mathcal{T}_{i+1}^\dagger \mathcal{T}_{i+1} \mathcal{T}_i, \tag{4}$$

where ε_T is the energy of a triplet with respect to the ground state, J_T is the hopping strength, and χ is the exchange (or density-density) interaction.

1.3 Singlet-triplet interaction

The singlet-triplet interaction (γ) couples pairs of neighbouring triplets to a singlet exciton,

$$H_{\text{int}} = \sum_{i=1}^N \gamma \left(\mathcal{T}_i^\dagger \mathcal{T}_{i+1}^\dagger \mathcal{S}_i + \mathcal{T}_i^\dagger \mathcal{T}_{i+1}^\dagger \mathcal{S}_{i+1} + h.c. \right). \tag{5}$$

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[1] The subscript ex represents the fact that this is the Hamiltonian for the excitons, i.e, the excited electronic states of the system.
[2] We have here collapsed the 3-dimensional triplet manifold (space of states) into a unique state $|T_1\rangle$ [1, 2], since we will not consider any magnetic field that can break their degeneracy via the Zeeman interaction.

1.4 Disorder

Disorder in H_{ex} can affect all parameters, due to small variations in the energy gap between ground, singlet and triplet states, and in the orientation of the molecules with respect to each other, which affects the couplings between neighbouring sites.

When considering disorder, we are going to replace any system parameter α discussed above as follows

$$\alpha \rightarrow \alpha_i = \alpha + \delta_\alpha^{(i)}, \tag{6}$$

where $\delta_\alpha^{(i)}$ is sampled from a normal distribution with zero mean ($\mu_\alpha = 0$) and standard deviation σ_α.

2 Dynamics and observables

2.1 Dynamics

We will consider the dynamics of an initial out-of-equilibrium state $|\phi_0\rangle$ that is generated by H_{ex},

$$|\psi(t)\rangle = U(t)|\psi_0\rangle, \tag{7}$$
$$= e^{-iH_{\text{ex}}t}|\psi_0\rangle. \tag{8}$$

2.2 Number of triplets

To study the efficiency of singlet fission we will evaluate the number of triplets that are generated as a function of time in a singlet fission event, by calculating the expectation value $\langle \mathcal{N}_T \rangle_t = \langle \psi(t)|\mathcal{N}_T|\psi(t)\rangle$ of the total number of triplet operator $\mathcal{N}_T$,

$$\mathcal{N}_T := \sum_{i=1}^{N} \mathcal{T}_i^\dagger \mathcal{T}_i \ . \tag{9}$$

2.3 Singlet fission efficiency

Singlet fission efficiency $\eta(t)$ can be evaluated as

$$\eta(t) = \frac{\langle \mathcal{N}_T \rangle_t}{2\langle \mathcal{N}_S \rangle_t}, \tag{10}$$

where $\mathcal{N}_S := \sum_i \mathcal{S}_i^\dagger \mathcal{S}_i$ is the total number of singlet excitons. This is because the total Hamiltonian H_{ex} conserves the quantity,

$$\mathcal{C} := 2\mathcal{N}_S + \mathcal{N}_T. \tag{11}$$

When studying the efficiency we can also consider the time-averaged efficiency over a time interval τ,

$$\overline{\eta}(\tau) := \frac{1}{\tau} \int_0^\tau \eta(t) \, dt. \tag{12}$$

2.4 Initial state

Singlet fission begins after *photo-excitation*, i.e., after a photon is absorbed by the medium to form a singlet exciton. Singlets are usually delocalized due to hopping couplings J_S larger the the disorder σ_{ε_S} in the energetic landscape of the singlet-ground energy levels ε_S,

$$J_S > \sigma_{\varepsilon_S}. \tag{13}$$

Note that the singlet Hamiltonian conserves the number of singlets, i.e., $[\mathcal{N}_S, H_S] = 0$, which means that it can be decomposed into sectors with a fixed number of singlets

$$H_S = \sum_{n=0}^{N} H_S^{(n)}. \tag{14}$$

Let us consider the case where a photon is absorbed to form one singlet exciton ($n = 1$), so that we can select the sector $H_S^{(1)}$. Let us also consider negative hopping $J_S < 0$ such that $|J_S| < \varepsilon_S/2$. We will consider the initial state $|\psi_0\rangle$ given by the ground state of $H_S^{(1)}$. In the absence of disorder this state reads,

$$|\psi_0\rangle = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} \mathcal{S}_i^\dagger |S_0\rangle, \tag{15}$$

which has energy $\langle \psi_0|H_S|\psi_0\rangle = \varepsilon_S - 2|J_S|$ and is perfectly delocalized over the ring.

2.5 Resonant triplet-pair solution

The reference solution to the problem is given by the *resonant triplet-pair* solution, which is obtained for any value of γ and

$$J_S < 0, \tag{16}$$

$$|J_S| < \frac{\varepsilon_S}{2}, \tag{17}$$

$$\varepsilon_T = \frac{\varepsilon_S}{2} - |J_S|, \tag{18}$$

$$J_T = 0, \tag{19}$$

$$\chi = 0. \tag{20}$$

When the initial state is given by $|\psi_0\rangle$ as in Eq. (15), the number of triplets $\langle \mathcal{N}_T \rangle_t$ oscillates harmonically as

$$\langle \mathcal{N}_T \rangle_t = 2 \cos\left(4\gamma t + \pi\right) + 1. \tag{21}$$

3 Exciton-phonon interactions

Phonons are the excitations of vibrational modes of the lattice and of the molecules themselves. Here, we model vibrational modes as local harmonic oscillators that are linearly coupled to a local exciton operator. We will also consider only one vibrational mode per site and assume that a larger bath of vibrations interacts with each mode by inducing local excitation and de-excitations.

3.1 Exciton-phonon Hamiltonian

When we consider phonons the total Hamiltonian is

$$H = H_{\mathrm{ex}} + H_{\mathrm{ph}} + H_{\mathrm{ex-ph}}. \tag{22}$$

The phonons' Hamiltonian is given by

$$H_{\mathrm{ph}} = \sum_{i=1}^{N} \omega_0 a_i^\dagger a_i, \tag{23}$$

where ω_0 is the frequency of the vibrational modes and $a_i^\dagger$ the creation operator of the vibrational mode at site i.

The exciton-phonon interaction term is

$$H_{\mathrm{ex-ph}} = \sum_{i=1}^{N} g_S \mathcal{S}_i^\dagger \mathcal{S}_i \otimes \left(a_i^\dagger + a_i\right), \tag{24}$$

where g_S is the coupling between the exciton at site i and its vibrational mode.

Since harmonic oscillators are infinite dimensional, for numerical implementation we will truncate their Hilbert space to a maximum excitation m_{max}, so that their local dimension is $d_{\mathrm{ph}} = m_{\mathrm{max}}$.

3.2 Open system dynamics

When considering exciton-phonon interactions we will study the dynamics of the system starting from the following composite exciton-phonon initial state

$$|\Psi_0\rangle = |\psi_0\rangle \otimes \bigotimes_{i=1}^{N} |m=0\rangle_i, \tag{25}$$

where $|\psi\rangle$ is any initial exciton state, and $|m=0\rangle_i$ is the ground state of the local harmonic oscillator at site i.

The time evolution of this state is then propagated using the Gorini–Kossakowski–Sudarshan–Lindblad (GKSL) master equation [3, 4] to the exciton-phonon density operator $\dot{\rho}_t = \mathcal{L}[\rho_t]$,

$$\dot{\rho}_t = -i[H, \rho_t] + \mathcal{D}_{\mathrm{ph}}[\rho_t], \tag{26}$$

$$= -i[H, \rho_t] + \sum_{i=1}^{N} \sum_{k=\{+,-\}} \gamma_k \left(L_{i,k}\rho_t L_{i,k}^\dagger - \frac{1}{2}\{L_{i,k}^\dagger L_{i,k}, \rho_t\}\right), \tag{27}$$

where the Lindblad jump operators are $L_{i,+} = a_i^\dagger$ and $L_{i,-} = a_i$, i.e., the local creation and annihilation operators, with associated transition rates γ_+ and γ_-, respectively.

References

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