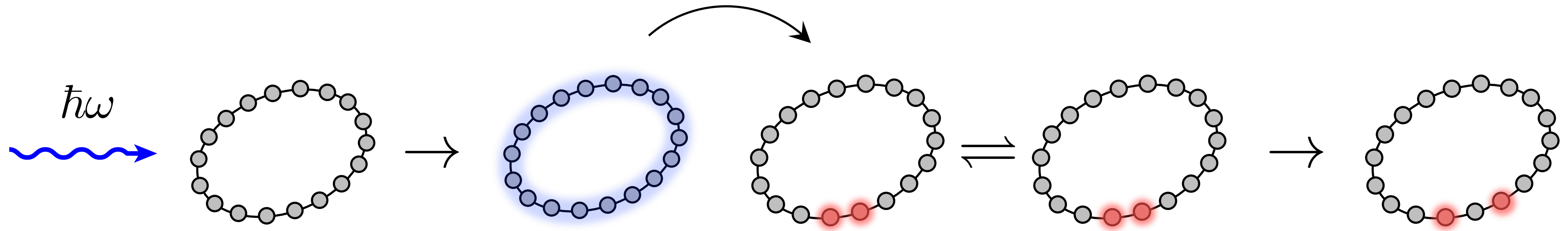
Francesco Campaioli

October 31, 2024 – Quantum Computing @ INFN

Optimisation of ultrafast singlet fission in 1D rings towards unit efficiency



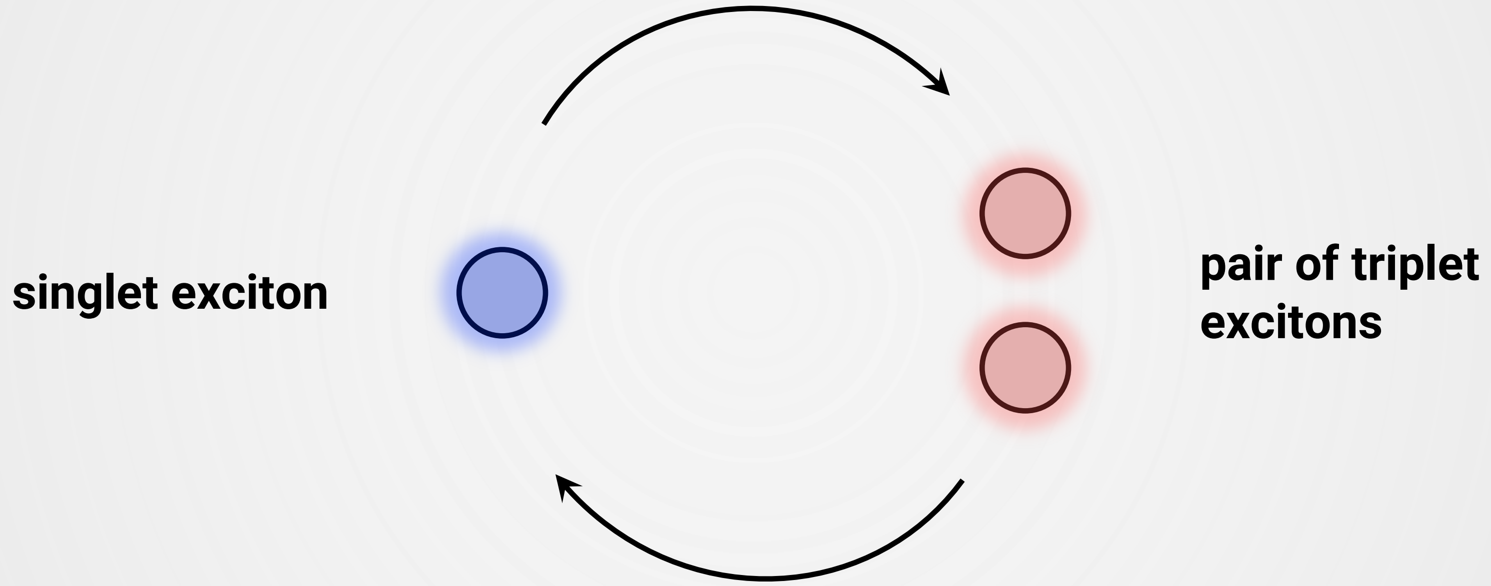
MSCA PF: 101063375 SpinSC | Spin-mediated spectral conversion for efficient photovoltaics

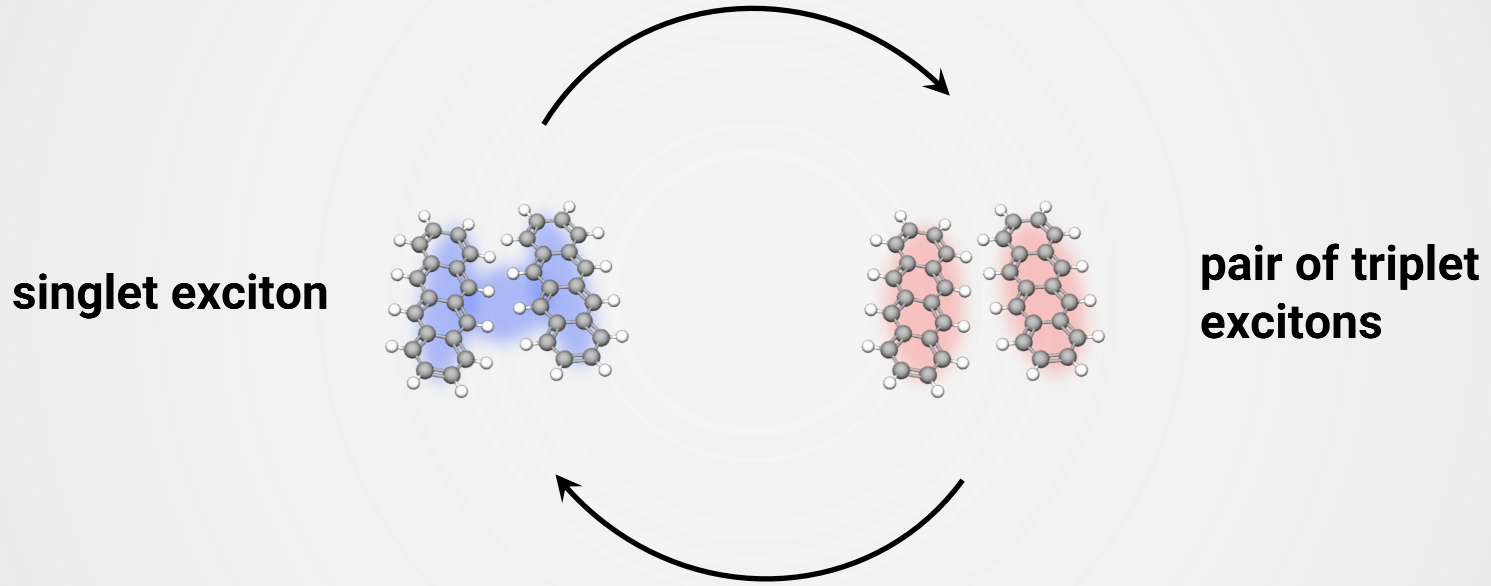
Funded by the European Union

MSCA

QUANTUM Information and Matter

Università degli Studi di Padova


singlet exciton
pair of triplet excitons


singlet exciton
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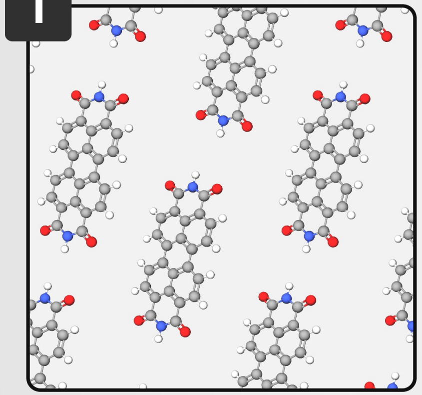
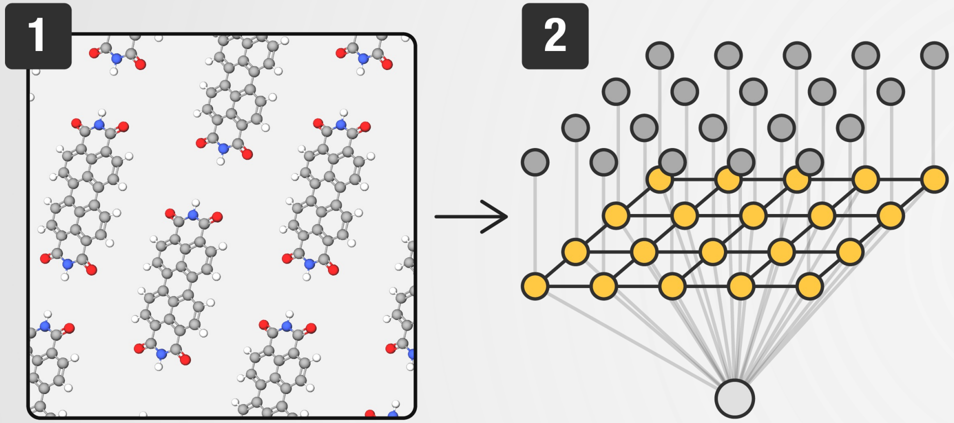
Quantum simulation for material optimisation

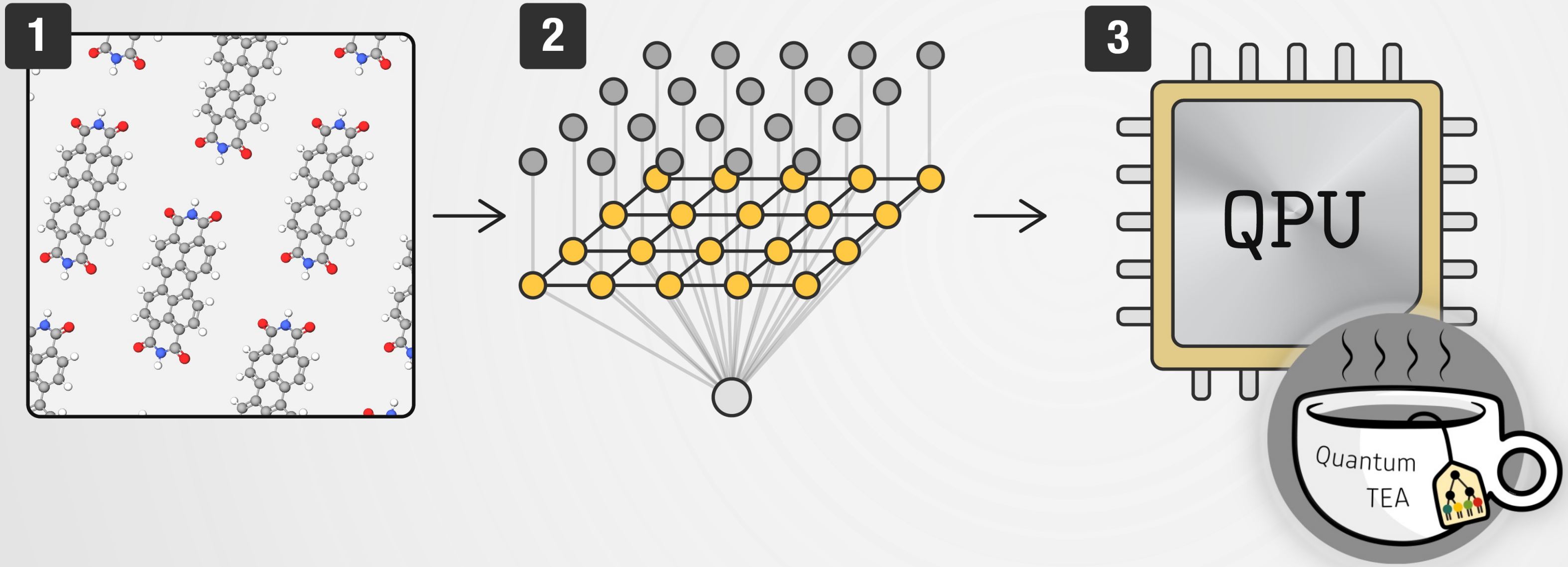
1



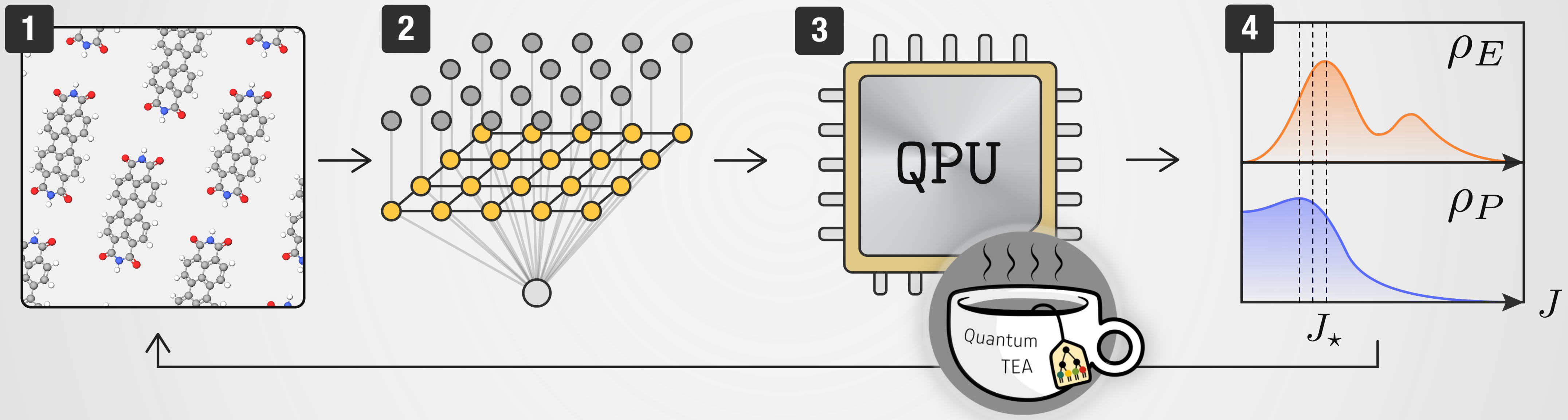
Quantum simulation for material optimisation

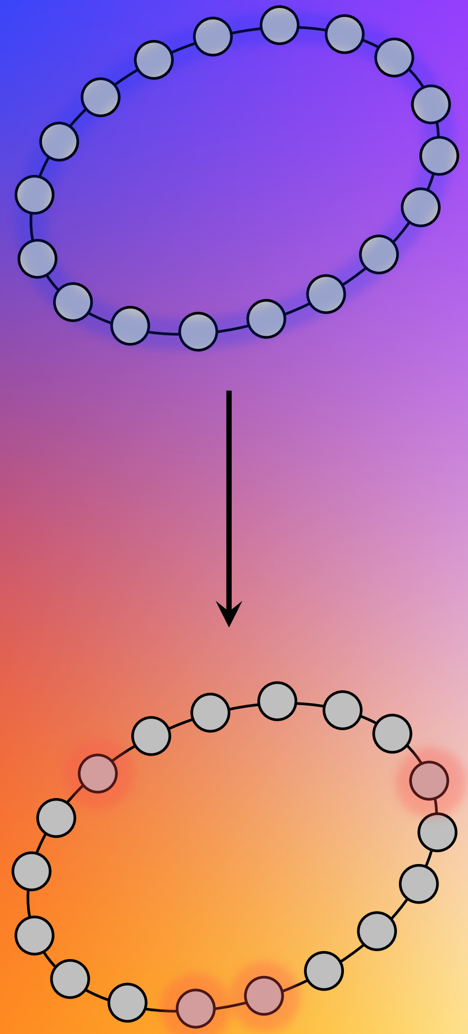


Quantum simulation for material optimisation



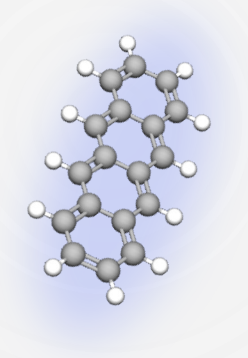
Quantum simulation for material optimisation





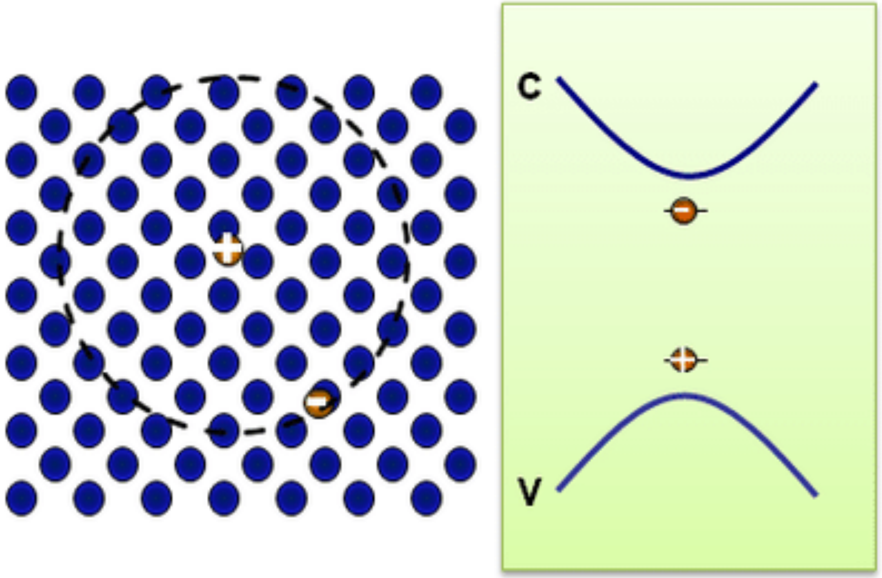
1. Excitons in organic semiconductors
2. Overview of singlet fission
3. Optimising singlet fission in 1D rings

1. Excitons in organic semiconductors

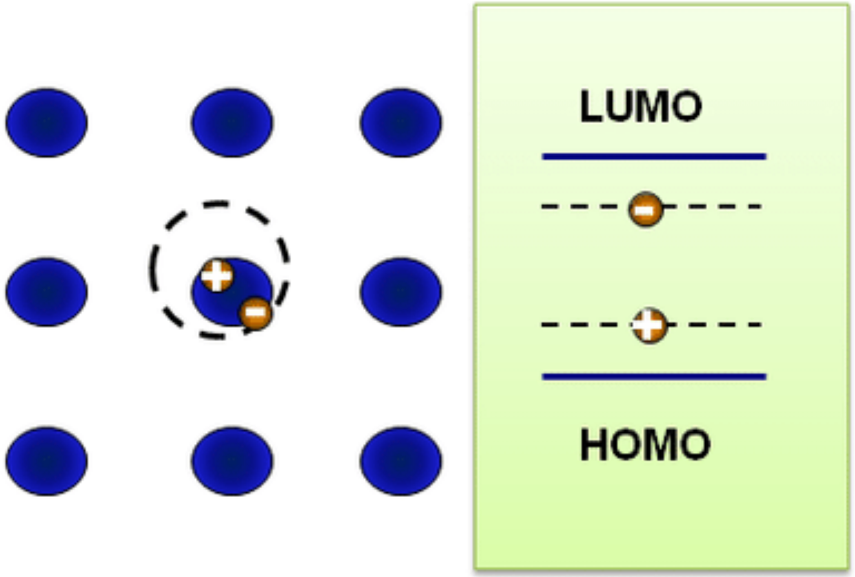


1. Excitons in organic semiconductors

Inorganic materials
Wannier-Mott excitons

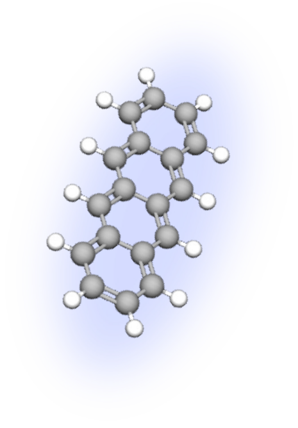


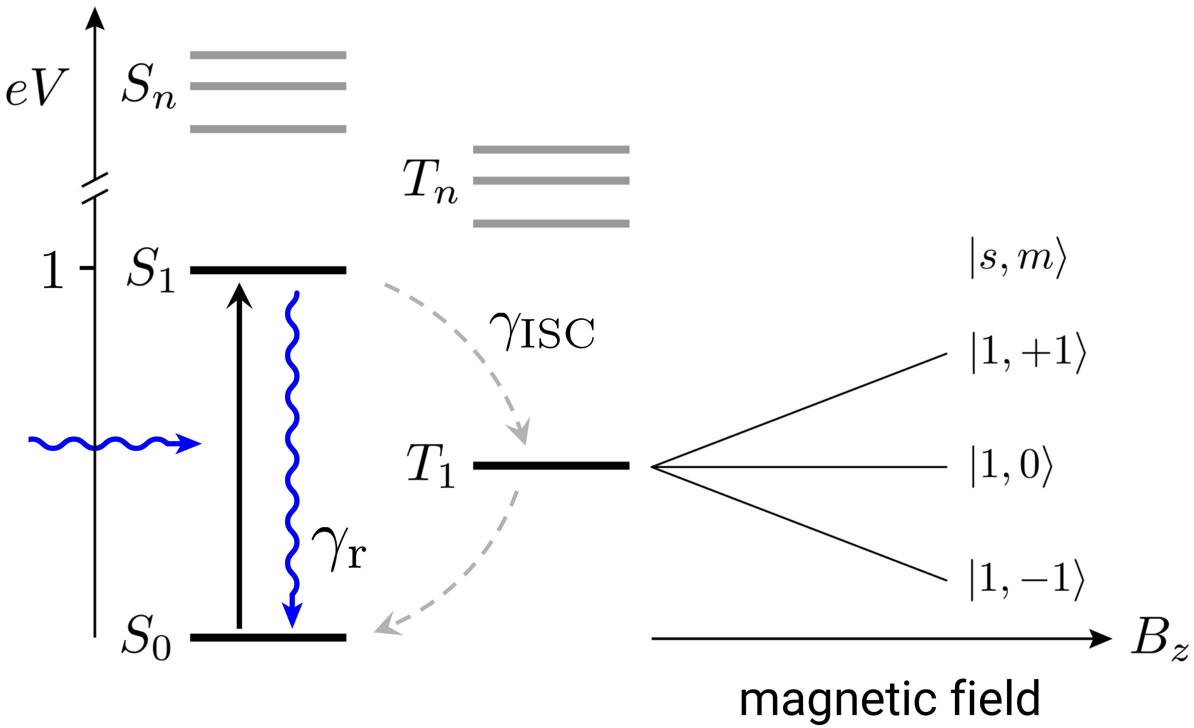
Organic materials
Frenkel excitons



1. Excitons in organic semiconductors

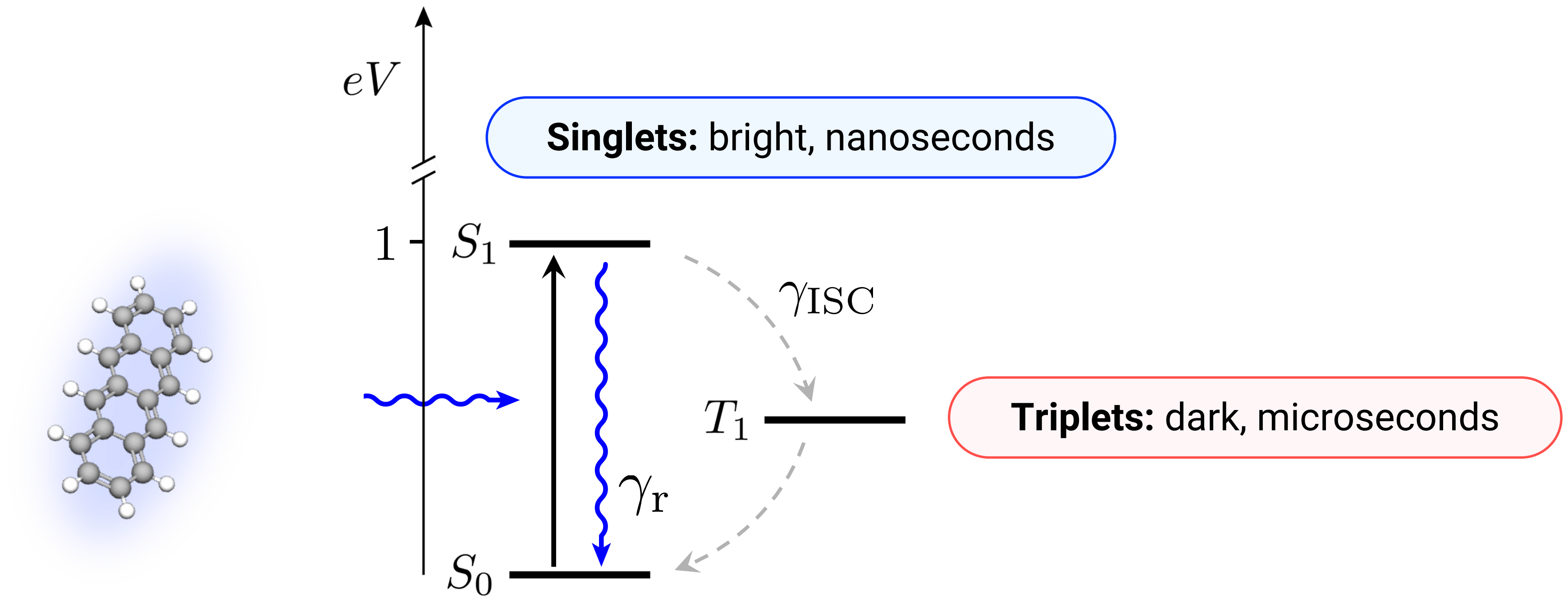
Excitons in organic molecules



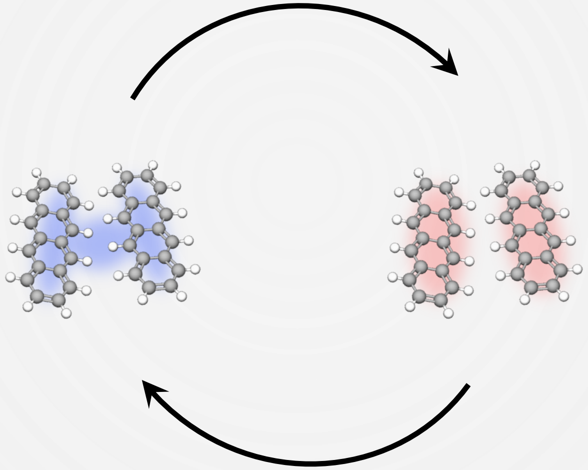


1. Excitons in organic semiconductors

Excitons in organic molecules



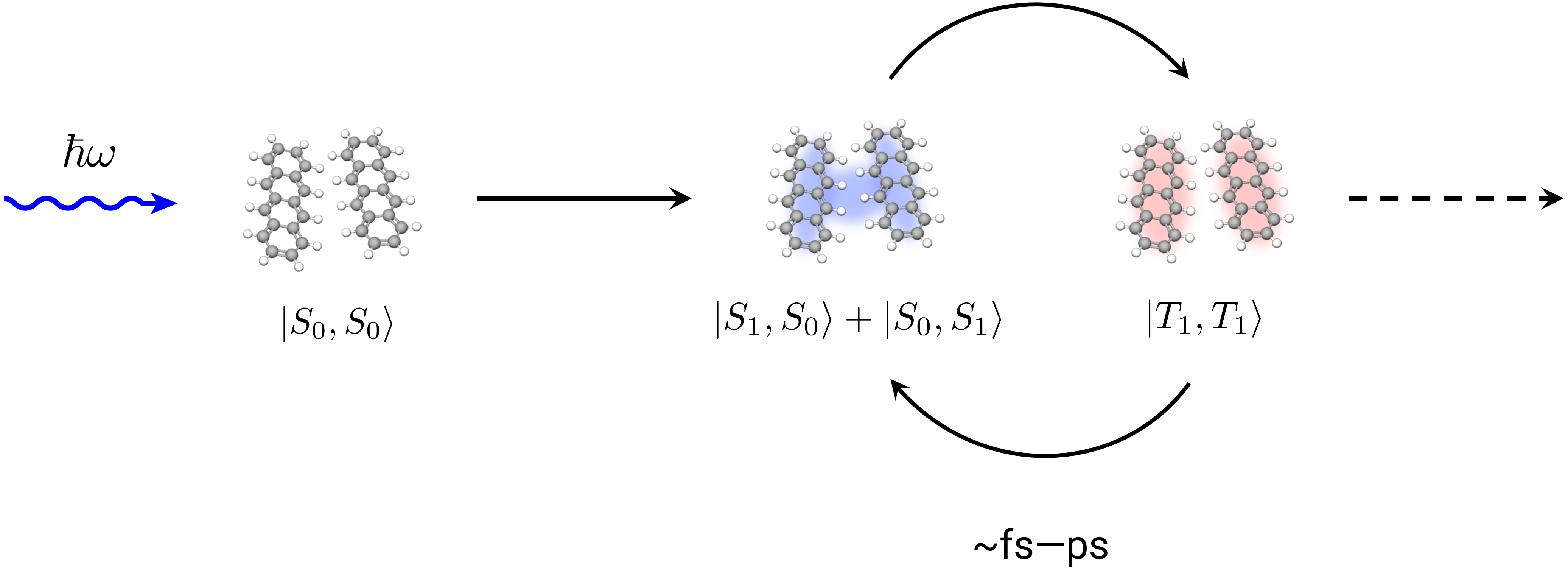
2. Overview of singlet fission



2. Overview of singlet fission

1. Photoexcitation

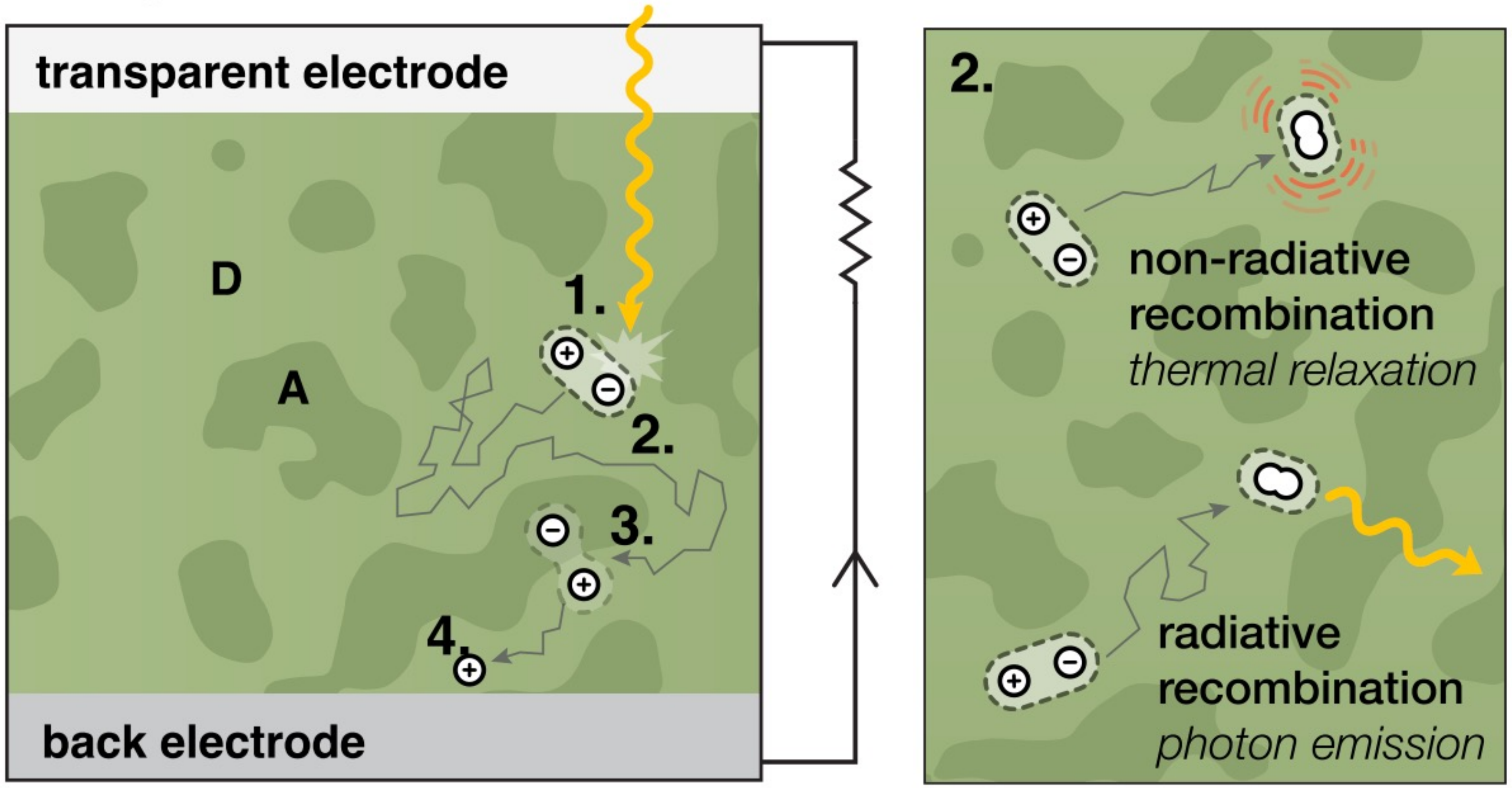
2. Ultrafast SF



2. Overview of singlet fission

$$H = H_{\mathrm{ex}} + H_{\mathrm{ph}} + H_{\mathrm{ex-ph}} \;\rightarrow\; \dot{\rho}_t = -i[H, \rho_t] + \mathcal{D}_\beta[\rho_t] \;\rightarrow$$

Exciton diffusion



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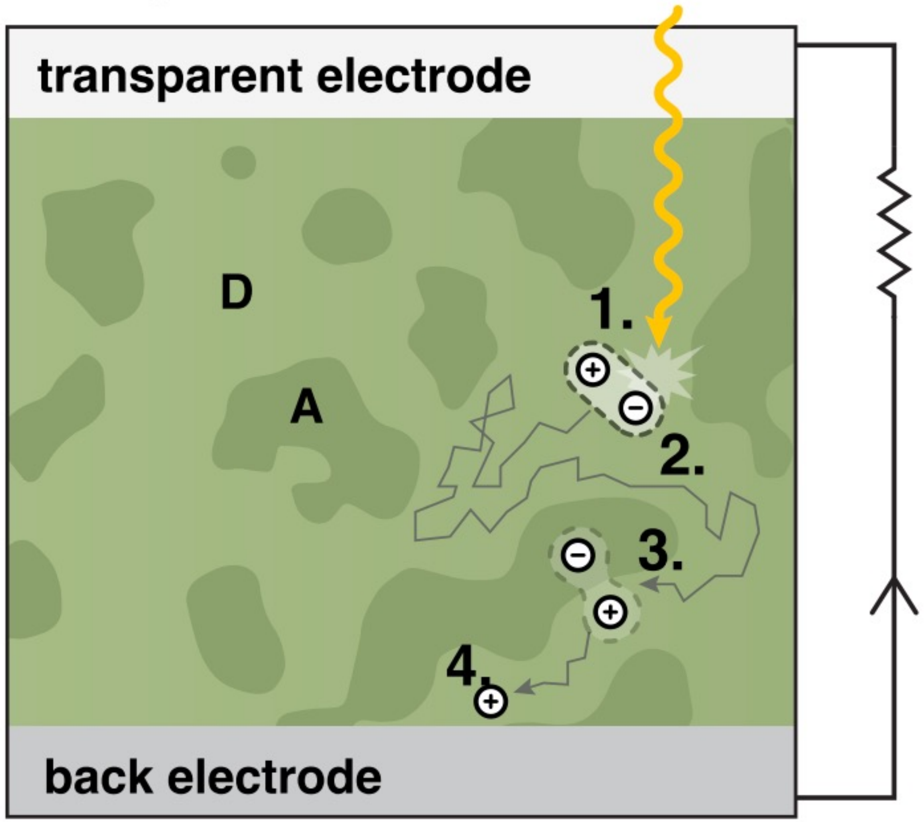
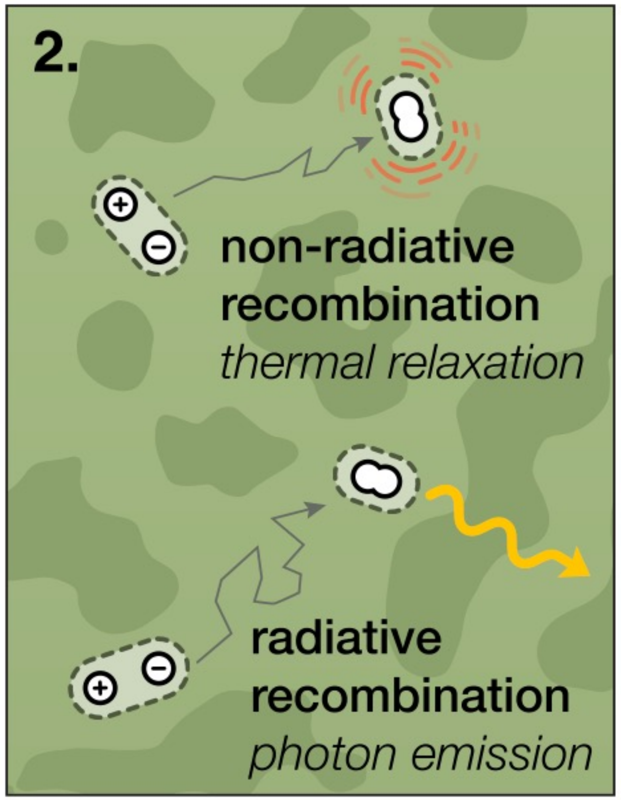
$$H = H_{\mathrm{ex}} + H_{\mathrm{ph}} + H_{\mathrm{ex-ph}} \;\rightarrow\; \dot{\rho}_t = -i[H, \rho_t] + \mathcal{D}_\beta[\rho_t] \;\rightarrow$$

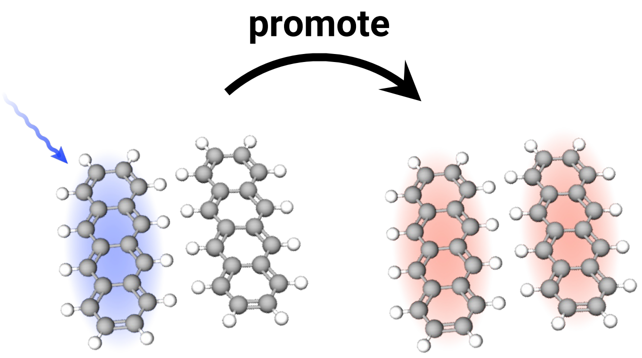
Exciton diffusion





Why singlet fission?

- 2 excitons per photon
- Singlets live nanoseconds
- Triplets live microseconds!

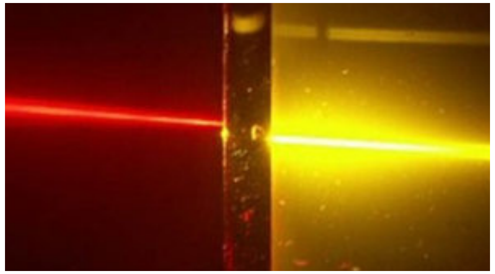


Nature Physics, volume 13, pages182–188 (2017) *J. Phys. Chem. Lett.* 2015, 6, 2367–2378 *ACS Energy Lett.* 2017, 2, 2, 476–480

2. Overview of singlet fission

Guidelines for optimal SF in organic materials

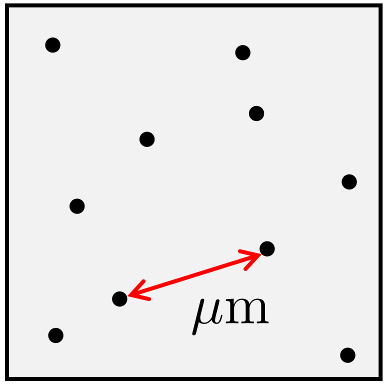
gas/liquid ✅



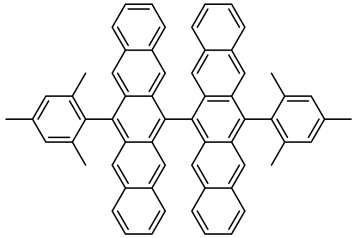
J. Phys. Chem. Lett. 2015, 6, 2367–2378

ACS Energy Lett. 2017, 2, 2, 476–480

low concentration ✅



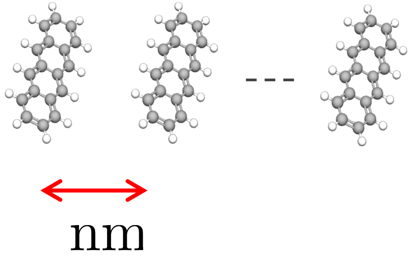
small correlated ✅



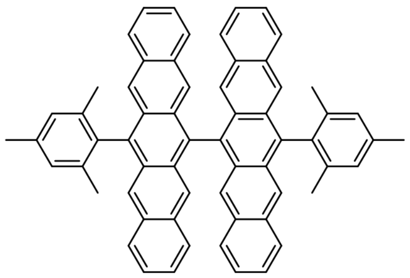
Nature Physics, volume 13, pages182–188 (2017)

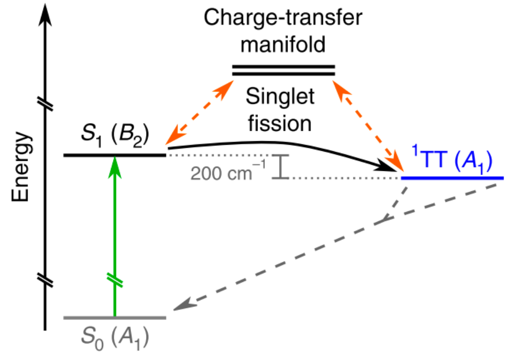
Nature Chemistry, volume 11, pages821–828 (2019)

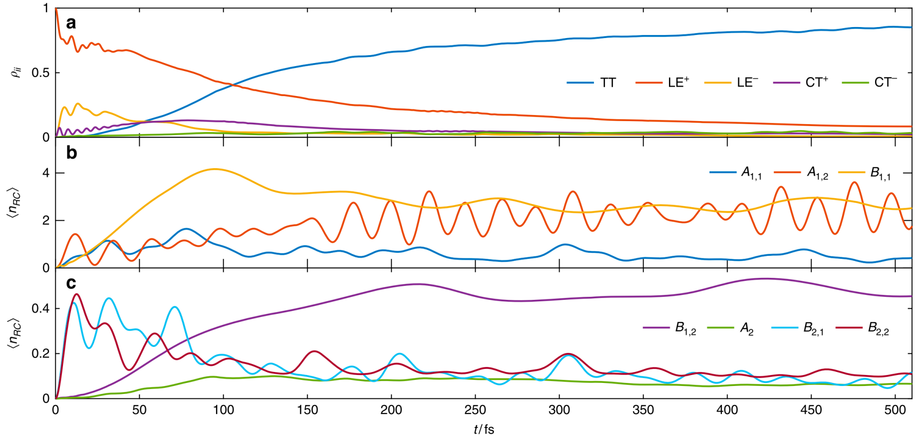
extended solids ?



Optimal SF in molecular dimers





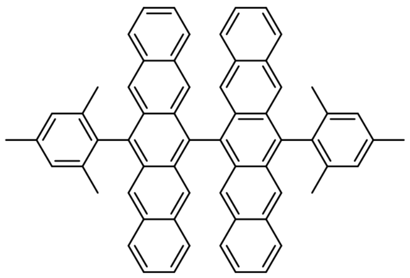


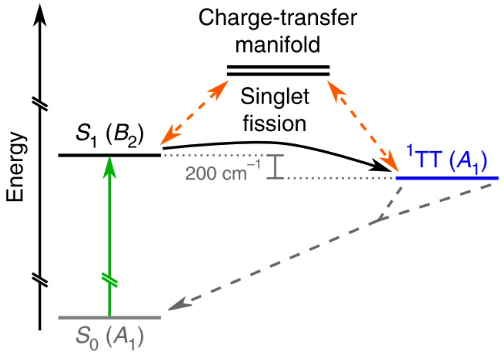
Nature Communications **10**, Article number: 4207 (2019)

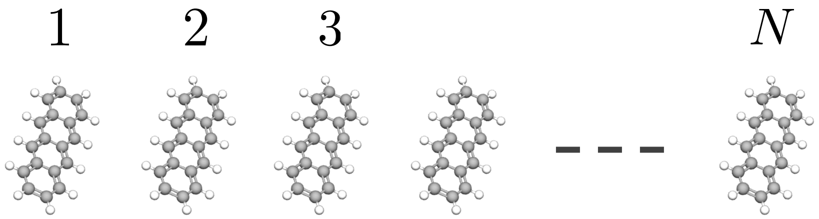
Nature Communications **10**, Article number: 1062 (2019)

2. Overview of singlet fission

Optimal SF in molecular dimers ⟶ Challenges in extended solids



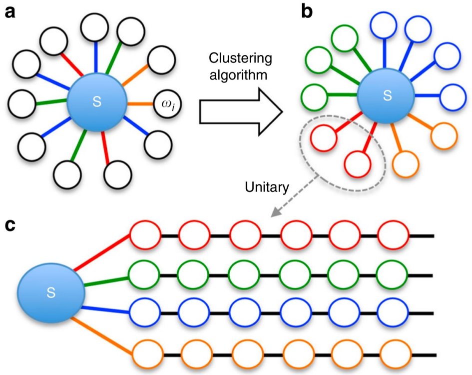




$$\dim\mathcal{H} \propto 3^N$$

Tree Tensor Networks with TDVP Dynamics

Non-perturbative exciton-phonon dynamics

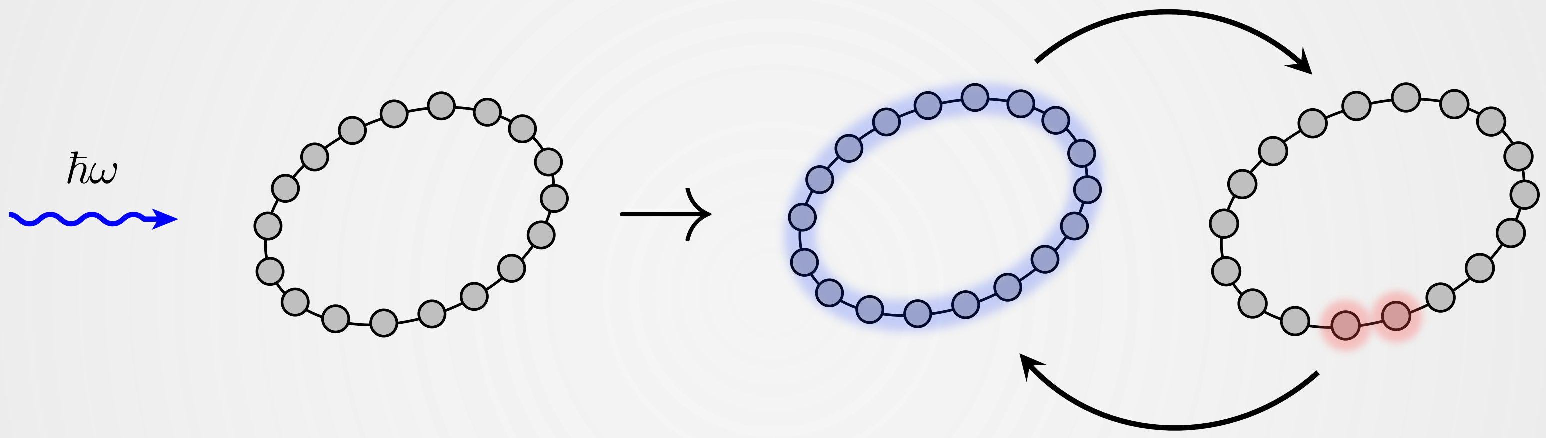


- Exciton delocalisation
- Exciton-exciton interactions
- Strong exciton-phonon couplings
- Non-Markovian exciton dynamics

Nature Communications **10**, Article number: 4207 (2019)

Nature Communications **10**, Article number: 1062 (2019)

3. Optimising singlet fission in 1D rings



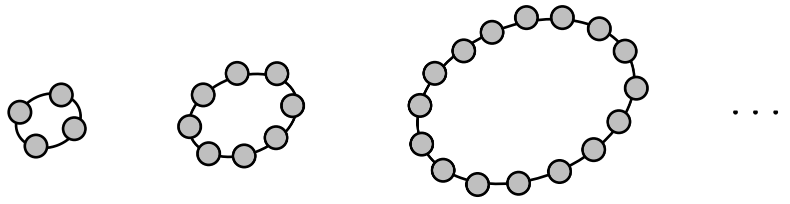
PRX Energy 3, 043003 – 30 October 2024

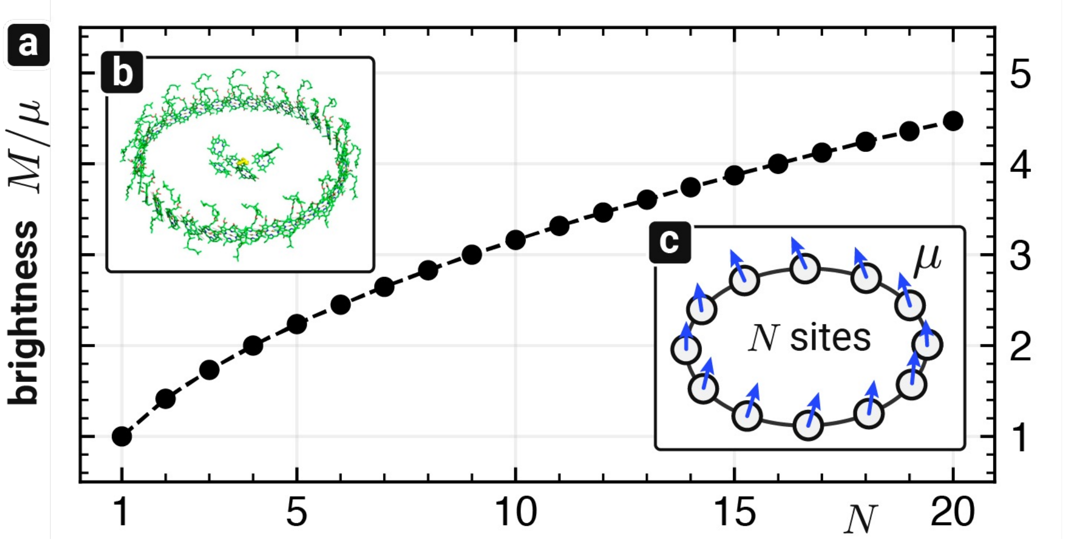
Optimisation of ultrafast singlet fission in 1D rings towards unit efficiency

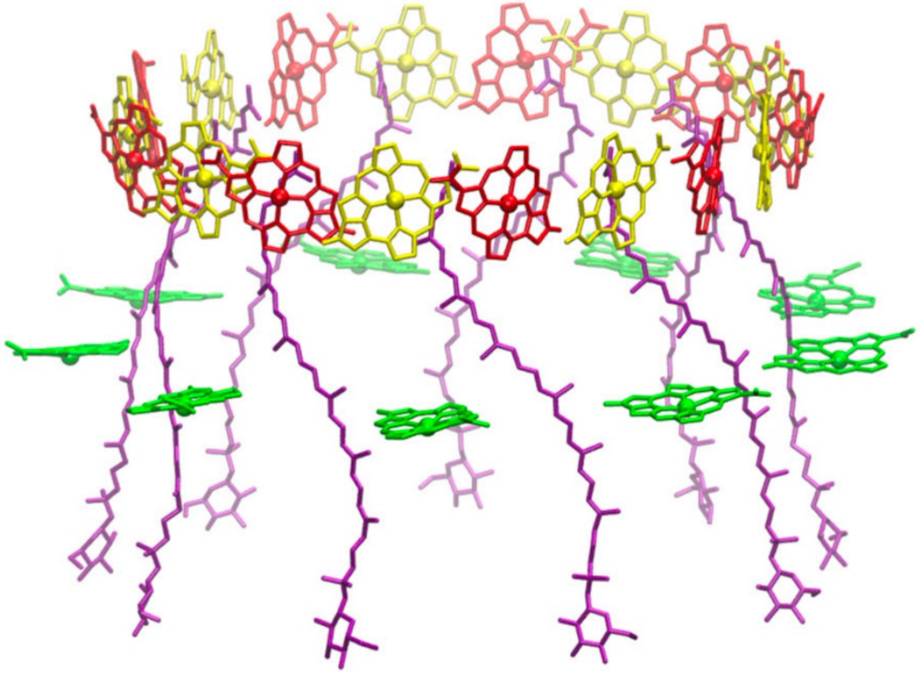
Francesco Campaioli, Alice Pagano, Daniel Jaschke, Simone Montangero

3. Optimising singlet fission in 1D rings

The system: 1D rings







Delocalized excitons in natural light-harvesting complexes

Seogjoo J. Jang and Benedetta Mennucci
Rev. Mod. Phys. **90**, 035003 – Published 21 August 2018

3. Optimising singlet fission in 1D rings

Many-body model of singlet fission

Excitons: $H_{\mathrm{ex}} = H_S + H_T + H_{\mathrm{int}}$

S₁ energy **S₁ hopping**

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

T₁ energy **T₁ hopping** **T₁T₁ interactions**

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

S1- T₁T₁ coupling

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

Conserved quantity

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

J. Chem. Phys. 143, 044118 (2015)

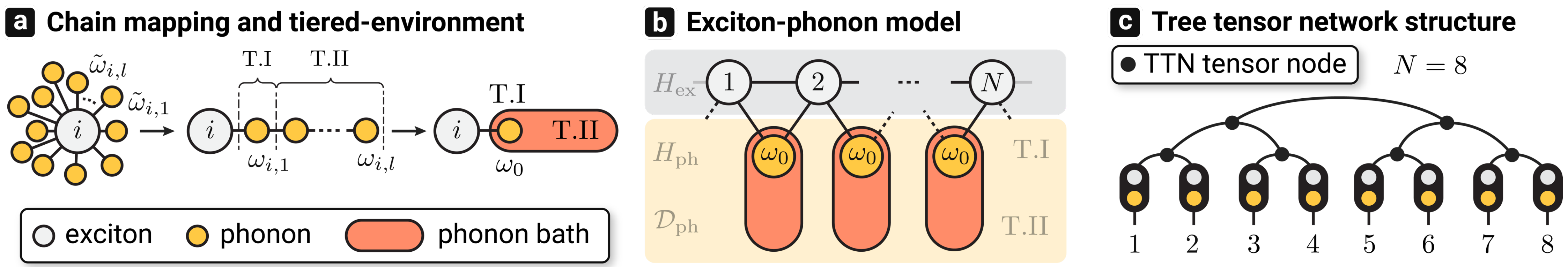
3. Optimising singlet fission in 1D rings

Open dynamics (exciton-phonon couplings)

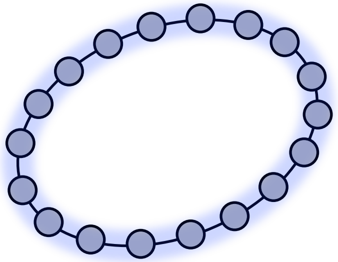
Vibrational modes: $H = H_{\mathrm{ex}} + H_{\mathrm{ph}} + H_{\mathrm{ex-ph}}$

$$H_{\mathrm{ph}} = \sum_{i=1}^{N} \sum_{l} \omega_{i,l} \hat{a}_{i,l}^{\dagger} \hat{a}_{i,l}$$

$$H_{\mathrm{ex-ph}} = \sum_{i=1}^{N} g_{i,l} A_{i,l} \otimes (\hat{a}_{i,l}^{\dagger} + \hat{a}_{i,l})$$



3. Optimising singlet fission in 1D rings



Initial state: bright (delocalised) singlet exciton

$$|\psi_0\rangle = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} \mathcal{S}_i^\dagger \bigotimes_{j=1}^{N} |S_0\rangle_j$$

1. Coherent exciton dynamics (no phonons)

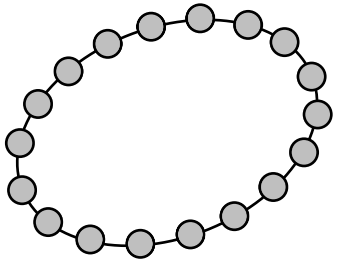
$$|\psi(t)\rangle = e^{-iH_{\mathrm{ex}}t}|\psi_0\rangle.$$

2. Open dynamics (exciton-phonon)

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

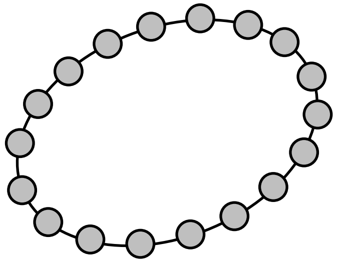
3. Optimising singlet fission in 1D rings

1. system

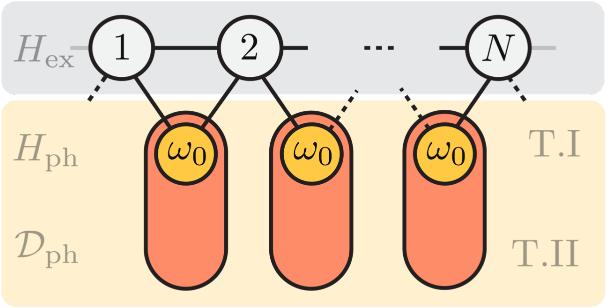


3. Optimising singlet fission in 1D rings

1. system

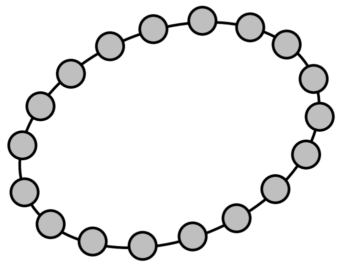


2. model



3. Optimising singlet fission in 1D rings

1. system



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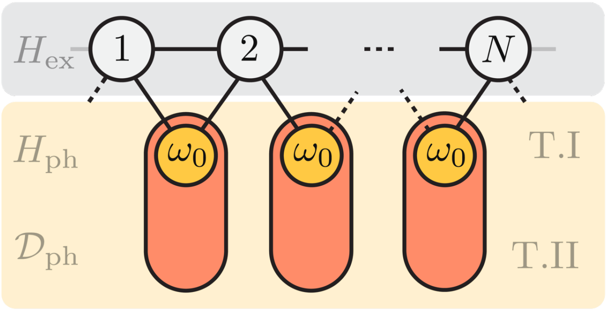
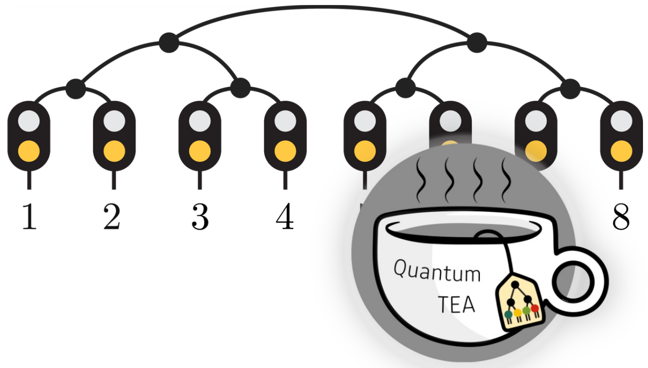
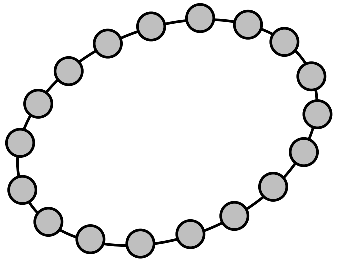


3. solver



3. Optimising singlet fission in 1D rings

1. system



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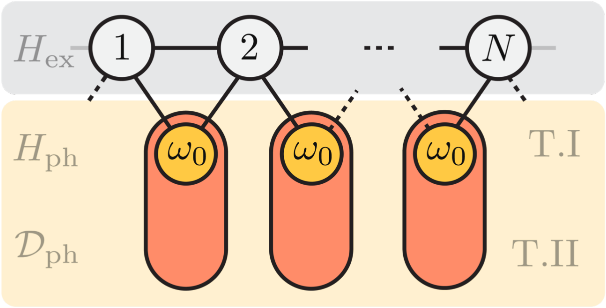

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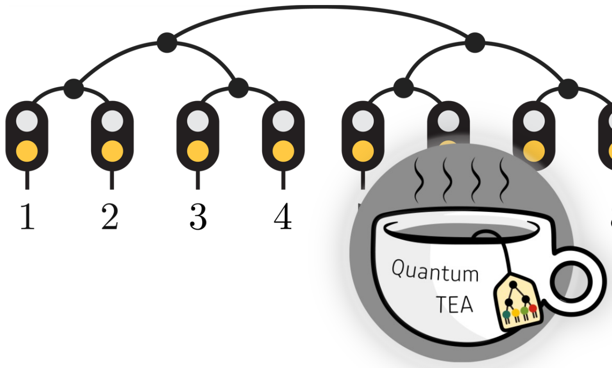
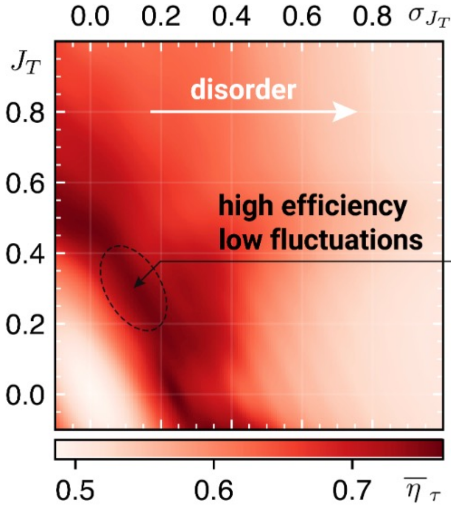


4. optimisation

$$\eta(t) := \frac{1}{2} \frac{\langle \mathcal{N}_T \rangle_t}{\langle \mathcal{N}_S \rangle_0}$$



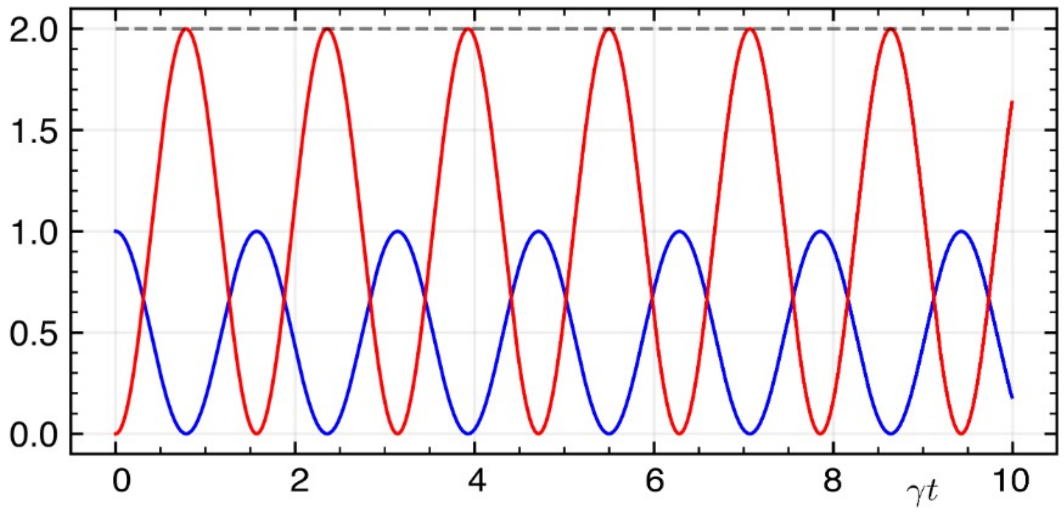
$$\mathcal{C} := 2\mathcal{N}_S + \mathcal{N}_T$$

3. Optimising singlet fission in 1D rings

Coherent exciton dynamics (no phonons)

Objective function: $\eta(t) := \frac{1}{2}\frac{\langle \mathcal{N}_T \rangle_t}{\langle \mathcal{N}_S \rangle_0}$

a **Resonant triplet-pair solution:** $\overline{\eta}_\tau = 0.50 \pm 0.35$



Parameters

$$-\varepsilon_S/2 < J_S < 0$$

$$\varepsilon_T = \frac{\varepsilon_S - 2|J_S|}{2} = 0.4 \qquad J_T,\ \chi = 0$$

3. Optimising singlet fission in 1D rings

Coherent exciton dynamics (no phonons)

Objective function: $\eta(t) := \frac{1}{2} \frac{\langle \mathcal{N}_T \rangle_t}{\langle \mathcal{N}_S \rangle_0}$

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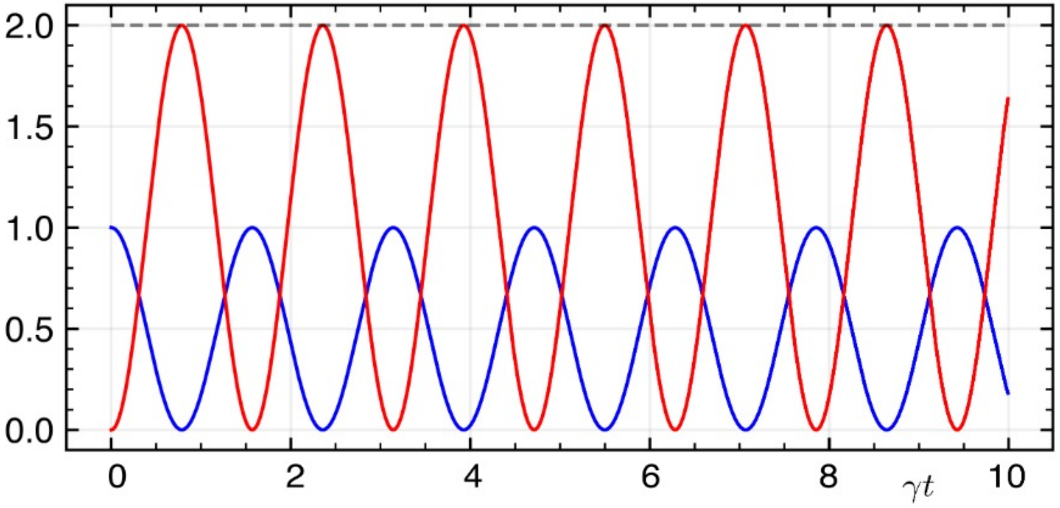
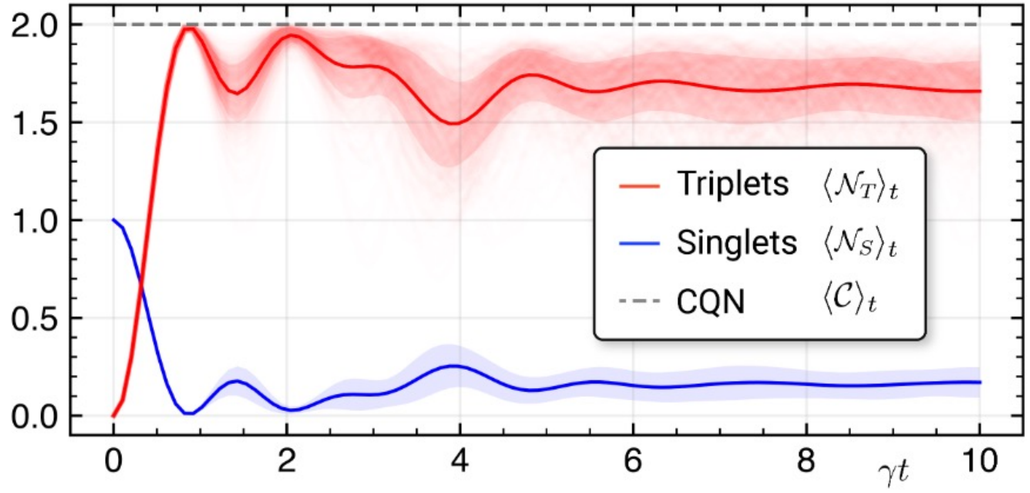


b **Optimised non-dissipative solution:** $\overline{\eta}_\tau = 0.85 \pm 0.04$



Parameters

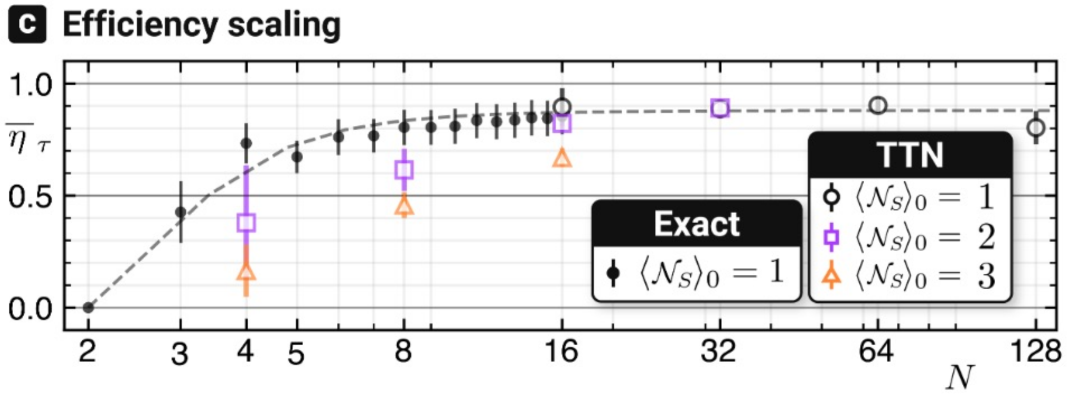
$-\varepsilon_S/2 < J_S < 0$

$\varepsilon_T = \frac{\varepsilon_S - 2|J_S|}{2} = 0.4 \qquad J_T,\ \chi = 0$

- Singlet delocalisation
- Fast triplets
- Repulsive triplet-triplet interaction
- Disorder in triplet hopping

3. Optimising singlet fission in 1D rings

Scaling with the system size

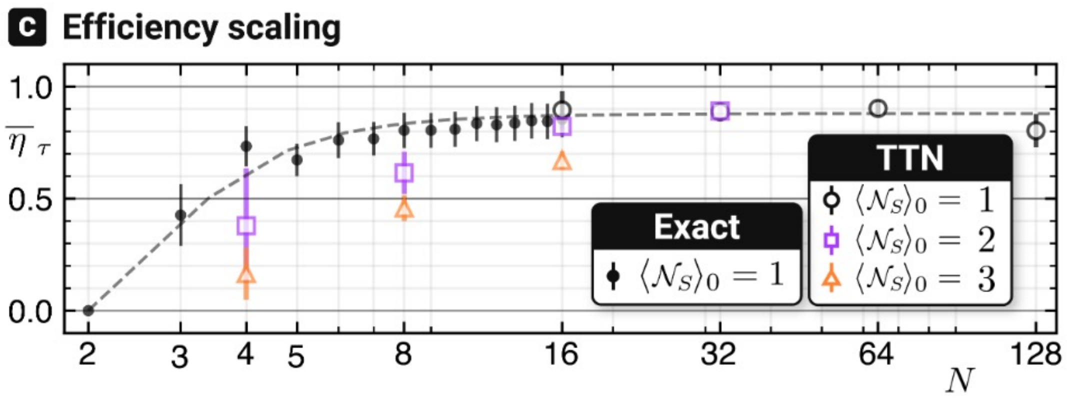


- **Singlet delocalisation** = more pairs of sites where to split

- **More sites** = triplet re-encounters are less likely

3. Optimising singlet fission in 1D rings

Scaling with the system size



- **Singlet delocalisation** = more pairs of sites where to split
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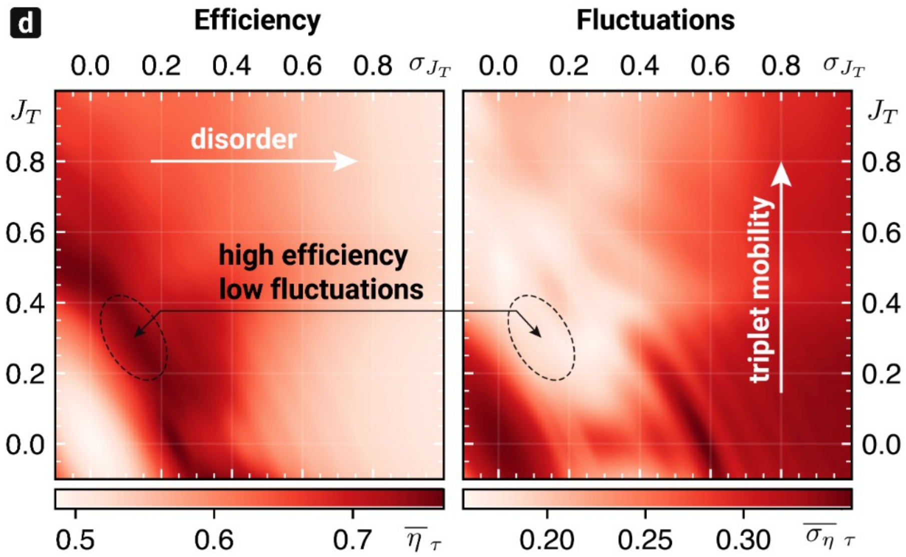
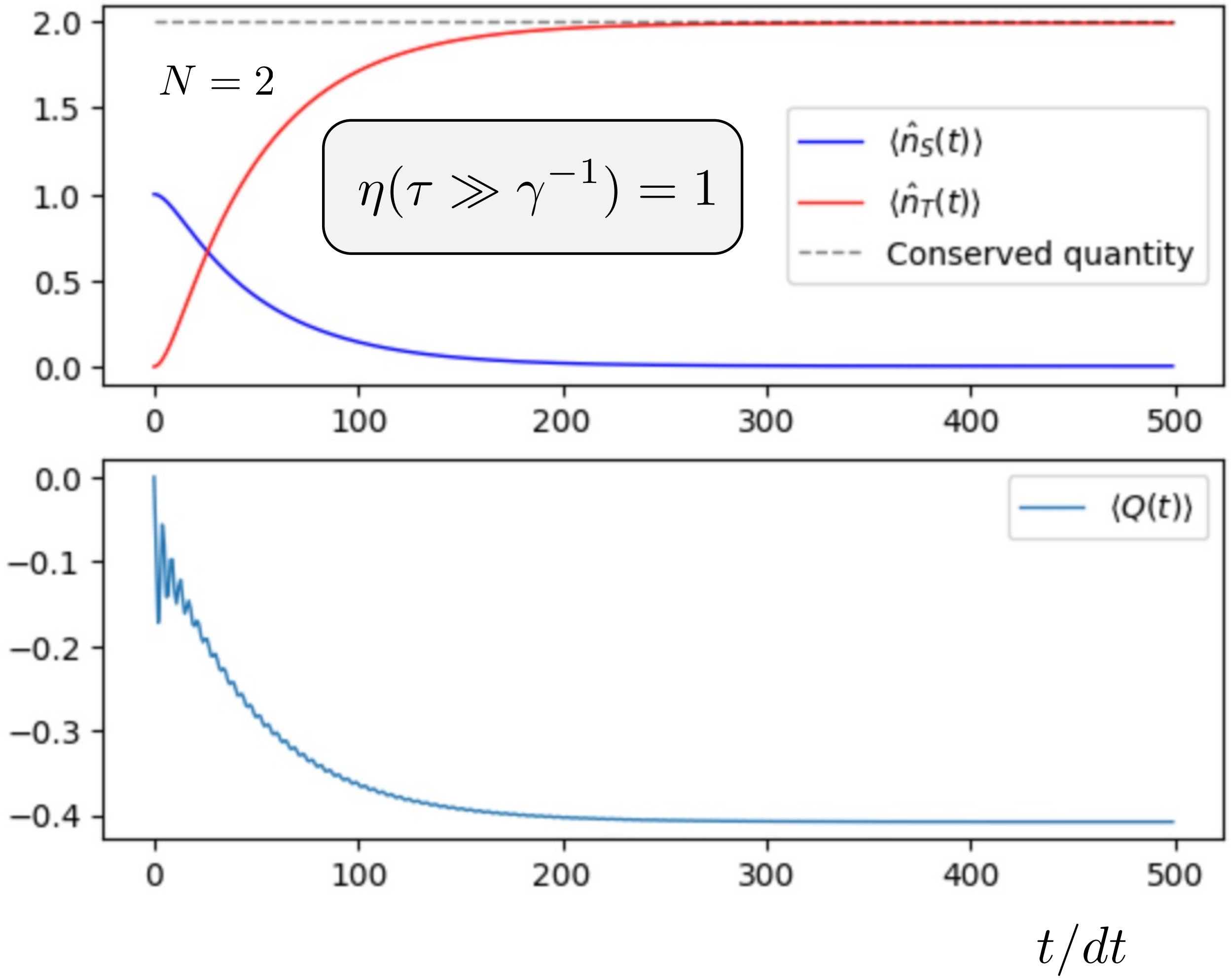
Effect of disorder

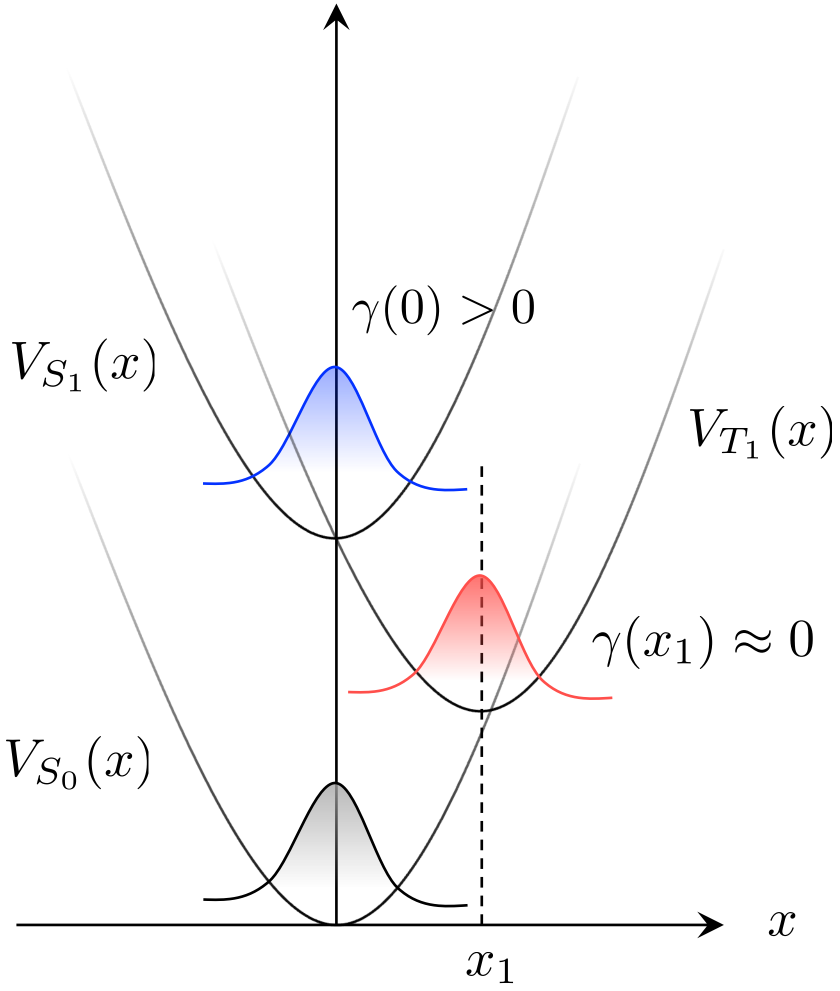


- **Poincare return theorem:** Initial singlet state must reform.
- Disorder makes recurrences less likely in the **ultrafast** time scale.

3. Optimising singlet fission in 1D rings

Dissipative dynamics (exciton-phonon couplings)



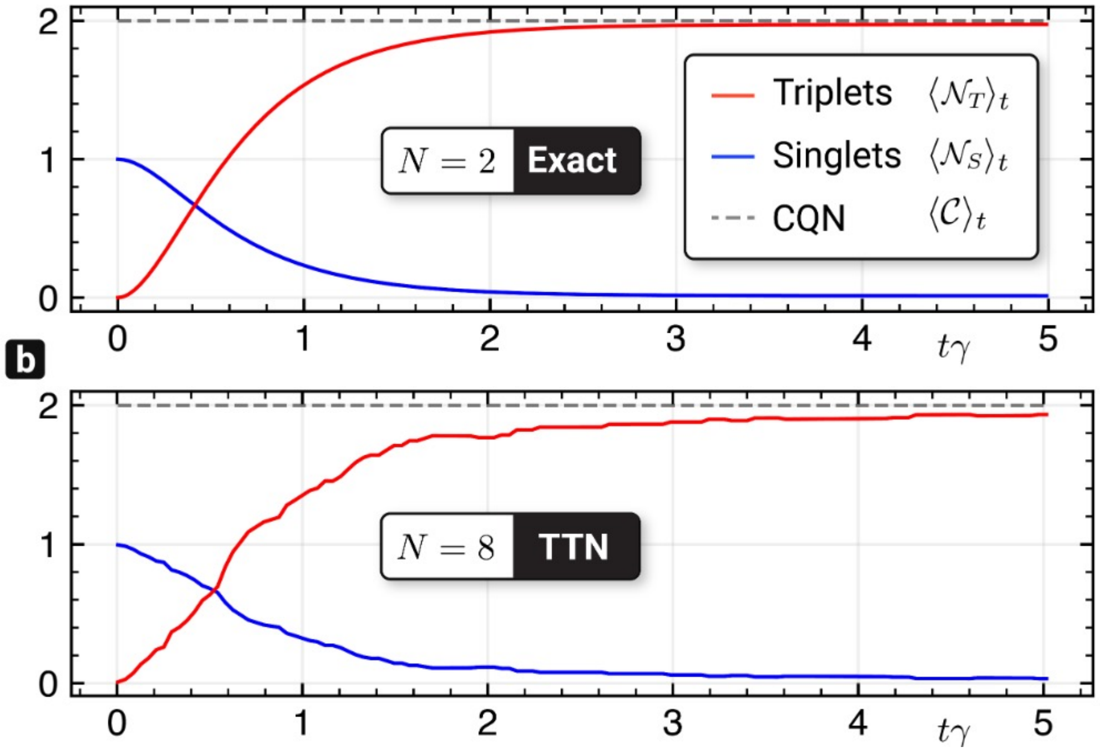


3. Optimising singlet fission in 1D rings

Dissipative dynamics (exciton-phonon couplings)

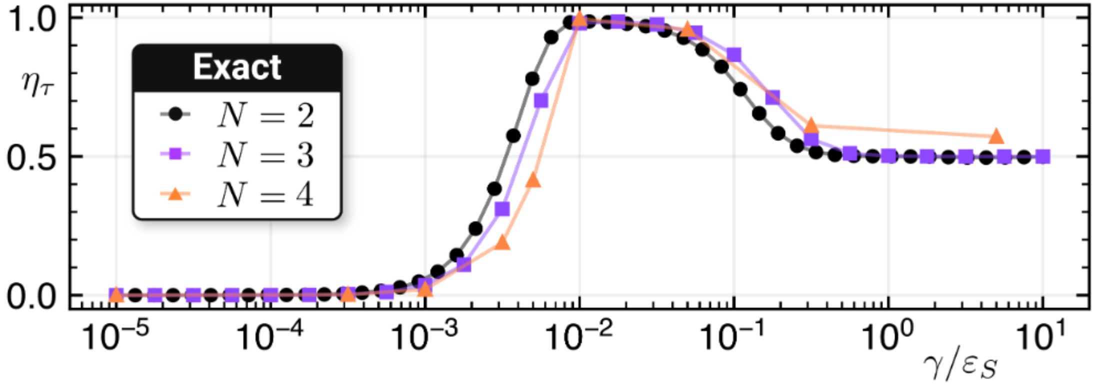
a **Optimised dissipative solution**

b



Can reach 100% efficiency

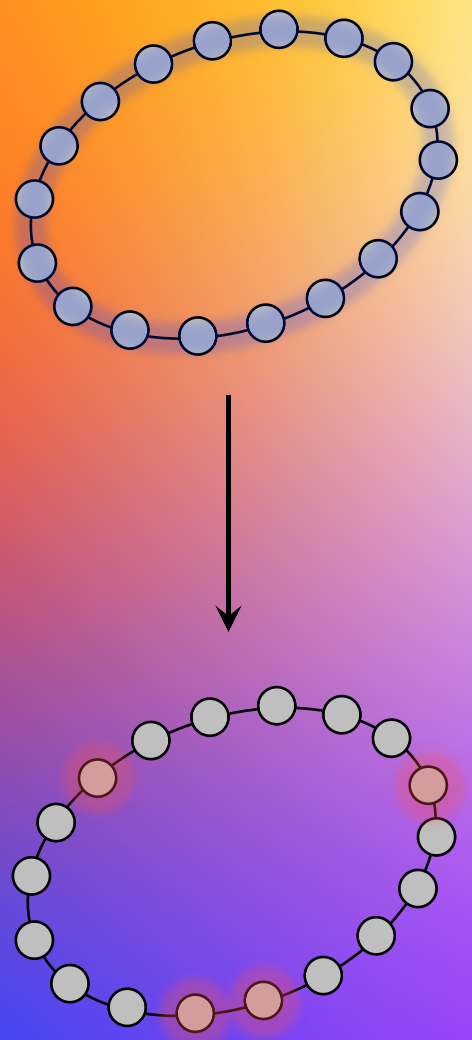
c **Efficiency beyond perturbative regime**



- **Why non-perturbative approach:** Efficiency depends on coupling strength

- **Computationally demanding:** Equivalent number of qubits

$$N_{\text{qbit}} = N \log_2(d_{\text{ex}} d_{\text{ph}})$$



Summary

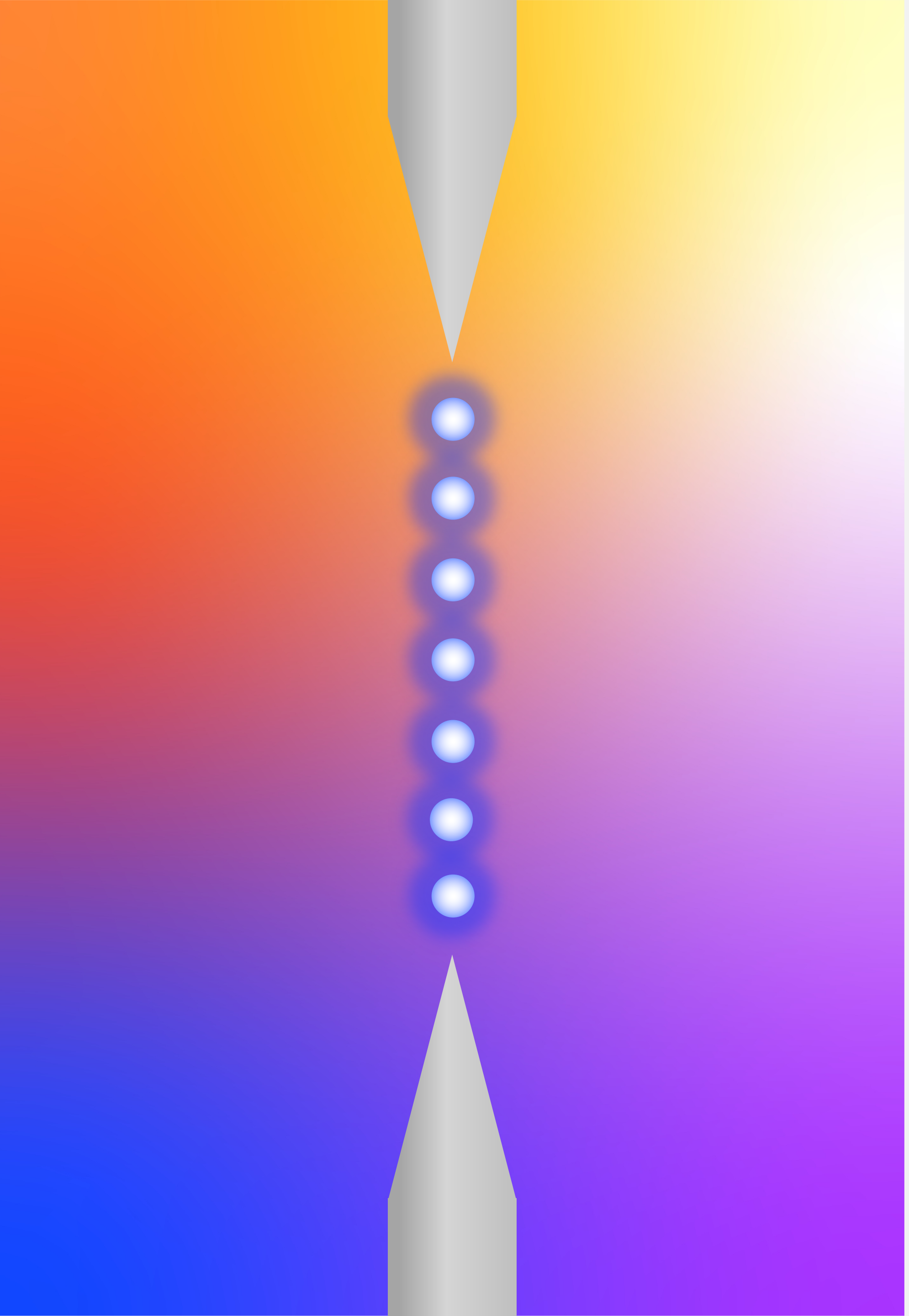
Singlet fission efficiency in extended solids increases with:

- singlet delocalization,
- triplet-triplet repulsive interaction,
- disorder in triplet hopping.

If exciton-phonon couplings can be tuned, unit efficiency maybe achieved.

Outlooks

- Towards thin films (2D) and molecular crystal (3D)
- Optimisation of other optoelectronic devices
- Quantum analog simulations



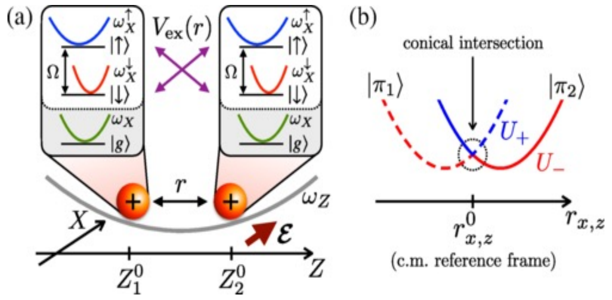
Trapped ion simulations of electron transfer

Article | Published: 28 August 2023

Direct observation of geometric-phase interference in dynamics around a conical intersection

C. H. Valahu, V. C. Olaya-Agudelo, R. J. MacDonell, T. Navickas, A. D. Rao, M. J. Millican, J. B. Pérez-Sánchez, J. Yuen-Zhou, M. J. Biercuk, C. Hempel, T. R. Tan & I. Kassal

Nature Chemistry **15**, 1503–1508 (2023) | Cite this article

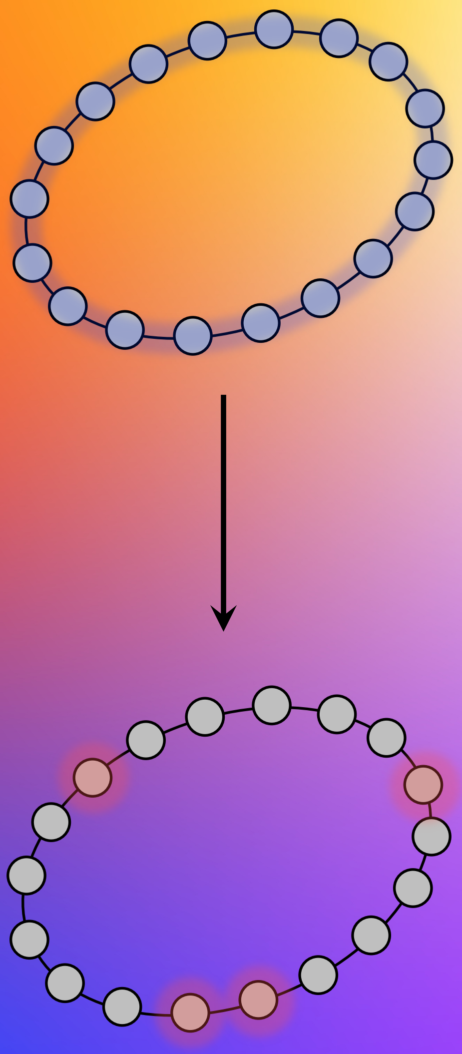


Phys. Rev. Lett. **126**, 233404 (2021)

Trapped-Ion Quantum Simulation of Electron Transfer Models with Tunable Dissipation

Visal So,[1,*] Midhuna Duraisamy Suganthi,[1,2,*] Abhishek Menon,[1] Mingjian Zhu,[1] Roman Zhuravel,[1] Han Pu,[1] Peter G. Wolynes,[1,3,4,5] José N. Onuchic,[1,3,4,5] and Guido Pagano[1,†]

arXiv: 2405.10368

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PRX Energy 3, 043003 – 30 October 2024

Optimisation of ultrafast singlet fission in 1D rings towards unit efficiency

Francesco Campaioli, Alice Pagano, Daniel Jaschke, Simone Montangero

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Theme 3.

Theoretical and experimenal methods for quantum effects in energy processes.

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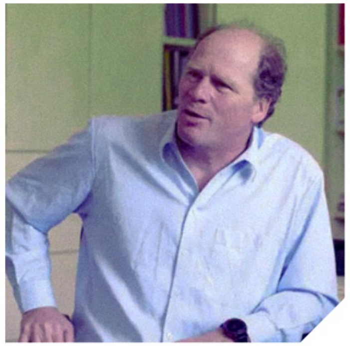

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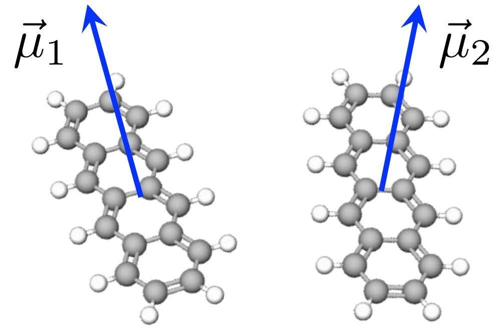
1. Excitons in organic semiconductors

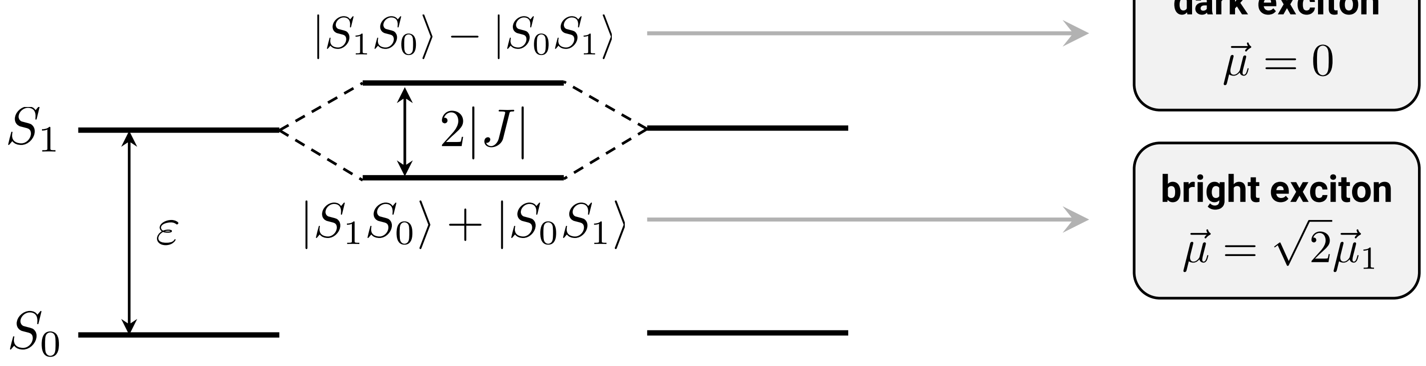
Exciton in molecular aggregates



$$J \propto \frac{\hat{\mu}_1 \cdot \hat{\mu}_2 - 3(\hat{r} \cdot \hat{\mu}_1)(\hat{r} \cdot \hat{\mu}_2)}{r^3}$$

J-aggregate

$$J < 0$$



1. Excitons in organic semiconductors

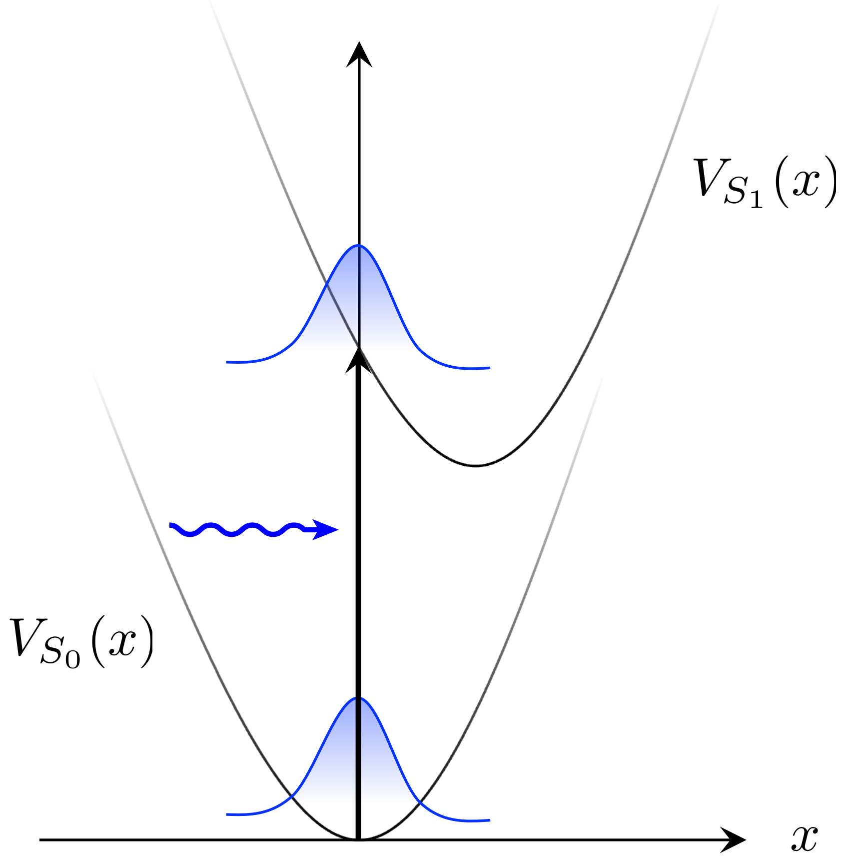
Exciton in molecular aggregates: Vibrational modes

$$H = H_{\text{ex}} + H_{\text{ph}} + H_{\text{ex-ph}}$$

$$= \frac{\varepsilon}{2}\sigma_z + \omega_0 a^\dagger a + \sum_k A_k \otimes (a^\dagger + a)$$

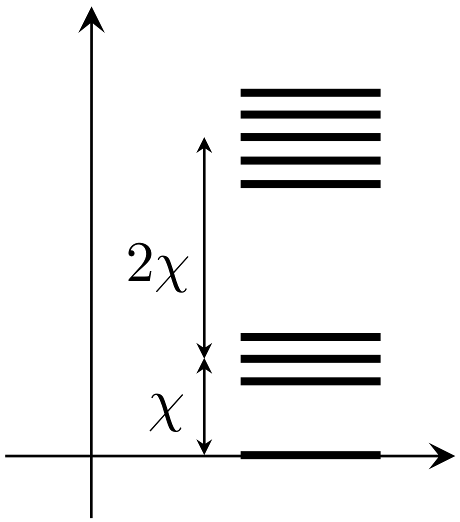
Franck-Condon Principle

$$|S_0\rangle \otimes |\varphi_0\rangle \to |S_1\rangle \otimes |\varphi_0\rangle$$



2. Overview of singlet fission

Triplet pair (9 states) $|1, m_1\rangle \otimes |1, m_2\rangle \to |^{2S+1}(TT)_M\rangle$ common basis for $[S_z, S^2] = 0$



"quintet states"

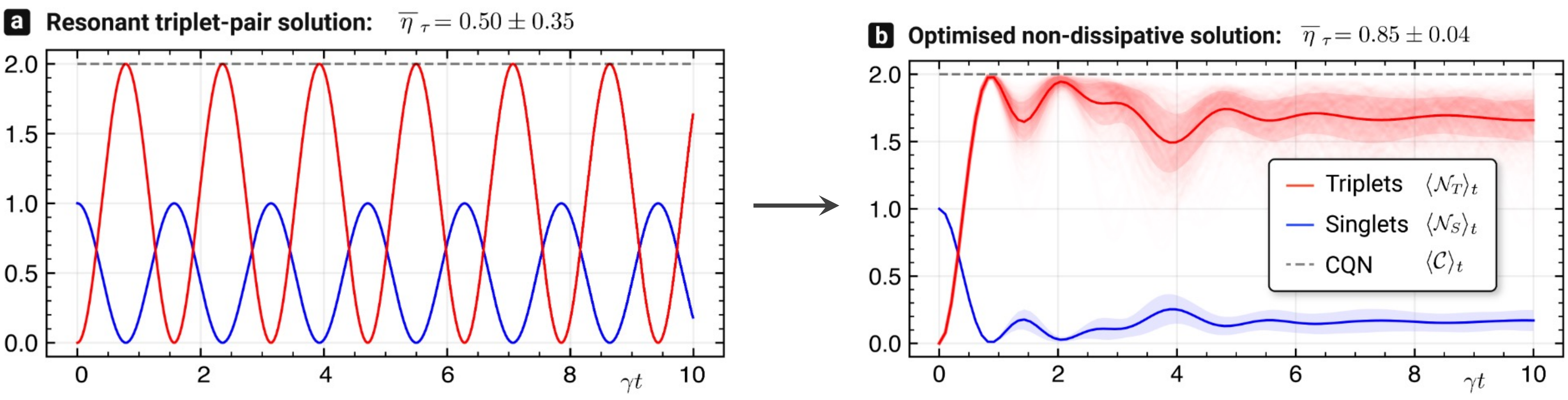
"triplet states"

"singlet state"

$|S_1\rangle \leftrightarrow |^1(TT)_0\rangle$ efficient when $\begin{cases} \Delta S = 0 \\ \Delta E \approx 0 \end{cases}$

$$|^1(TT)_0\rangle = \frac{1}{\sqrt{3}}\Big(|0,0\rangle - |-+\rangle - |+-\rangle\Big)$$

3. Optimising singlet fission in 1D rings



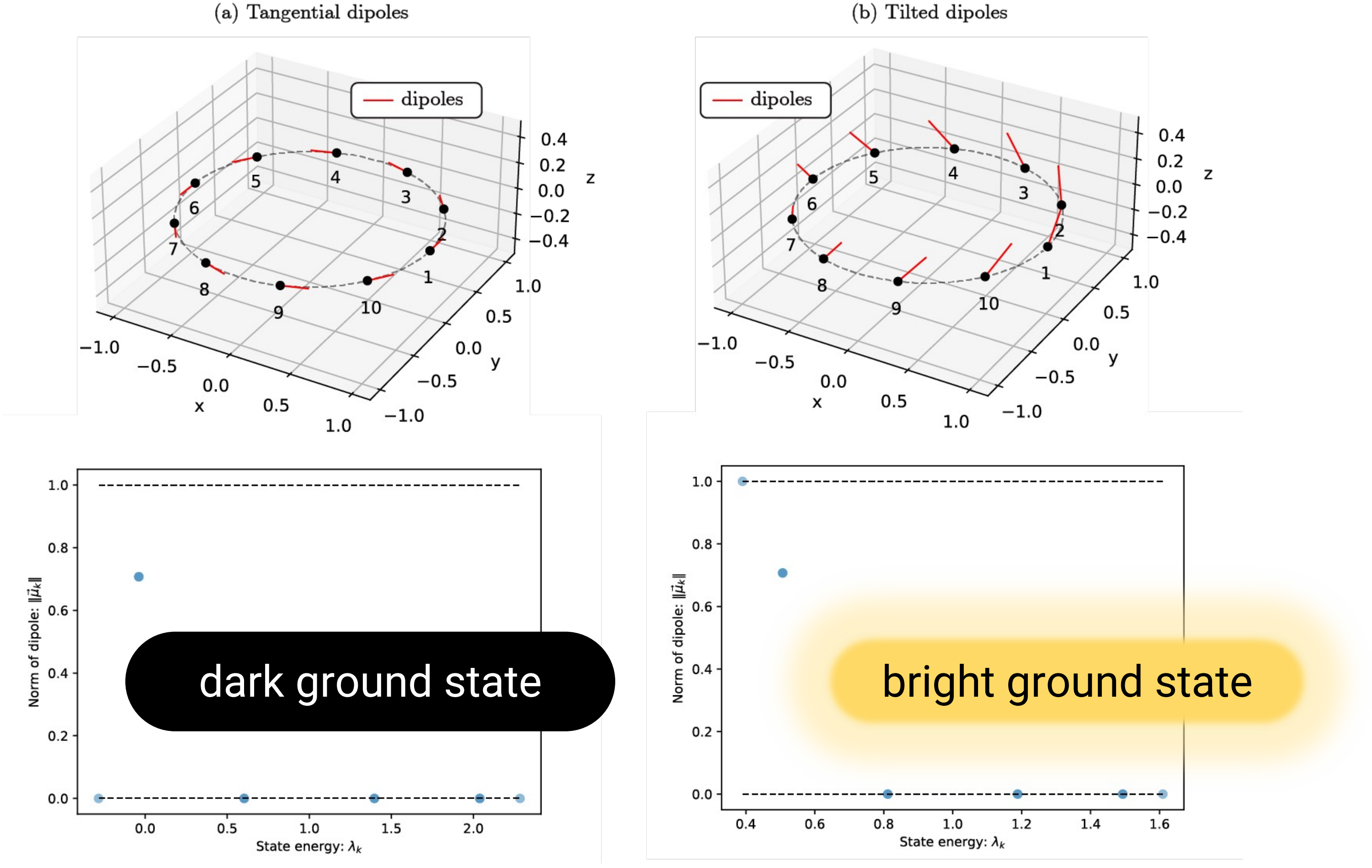
Model parameters, range, and solution efficiency

	ε_S	ε_T	J_S	J_T	χ	γ	σ_{J_T}	σ_χ	ω_0	x_0	g_S	g_T	η
Parameter range													
Minimum	1	0.35	-0.2	0	0	0.001	0	0	0	-0.1	0	0	
Maximum	1	0.65	0.2	0.5	0.3	0.6	0.2	0.2	0.5	0.1	0.5	0.5	
Solution													
Resonant triplet-pair	1	$\varepsilon_S/2 - \lvert J_S \rvert$	$J_S < 0$	0	0	γ	0	0	-	-	-	-	0.50 ± 0.35
Optimised non-dissipative	1	0.515	-0.001	0.3	0.068	0.437	0.114	0.005	-	-	-	-	0.85 ± 0.04
Optimised dissipative	1	0.372	-0.001	0	0	0.0103	0	0	0.25	-0.035	0	0.0038	0.99 ± 0.01

3. Optimising singlet fission in 1D rings

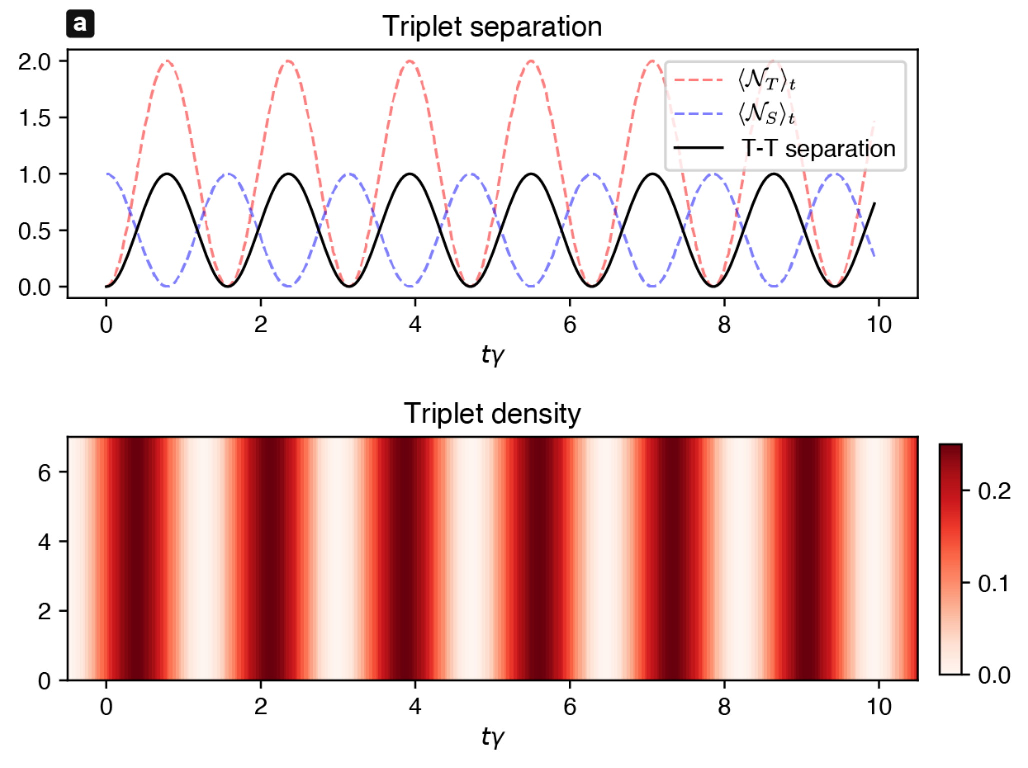
Brightness of singlet eigenstates

- tangentially aligned dipoles
- transverse dipoles
- tilted dipoles

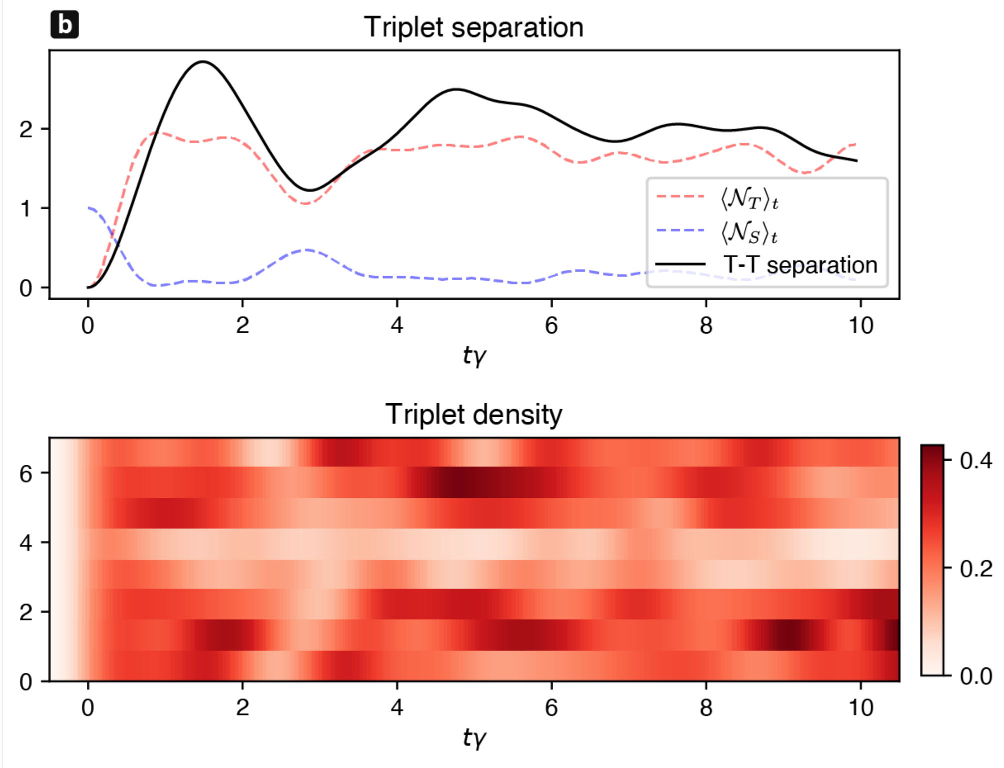


3. Optimising singlet fission in 1D rings

Triplet separation dynamics



limited separation = low efficiency



large separation = high efficiency