VISTA, 109, 2026, Groningen

Energy Transfer with a Twist: An Investigation of Chlorosome Lamella

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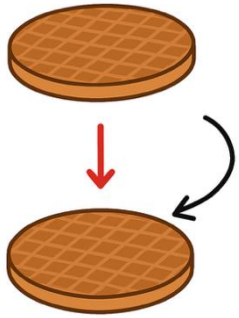
zernike institute for advanced materials

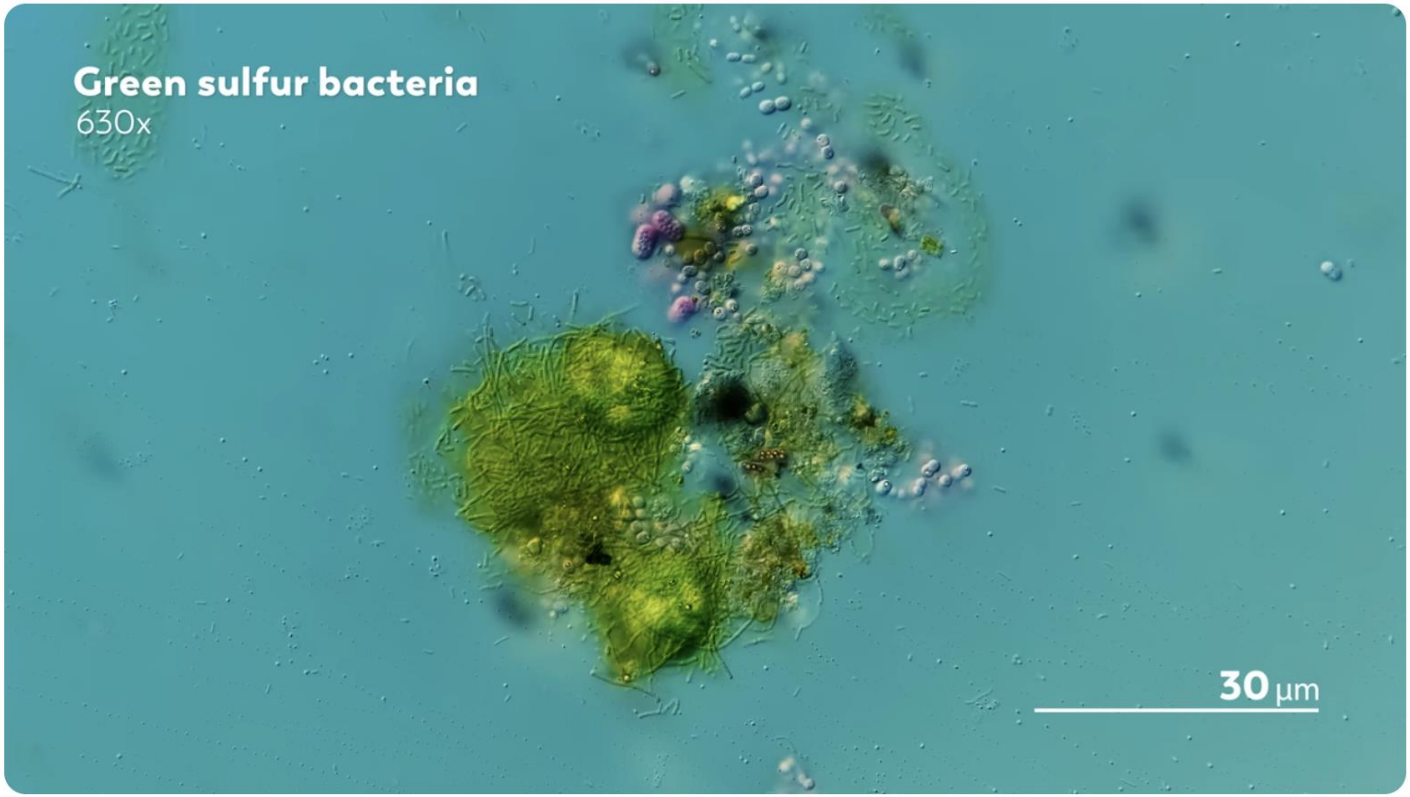
Outline

- Chlorosome Lamella
- MC-FRET
- The Lamella Twist
- The Manhattan Exciton Size
- Outlook



Yieon Park

Gijsbert ten Hoven



Is It Possible To Photosynthesize In The Dark?

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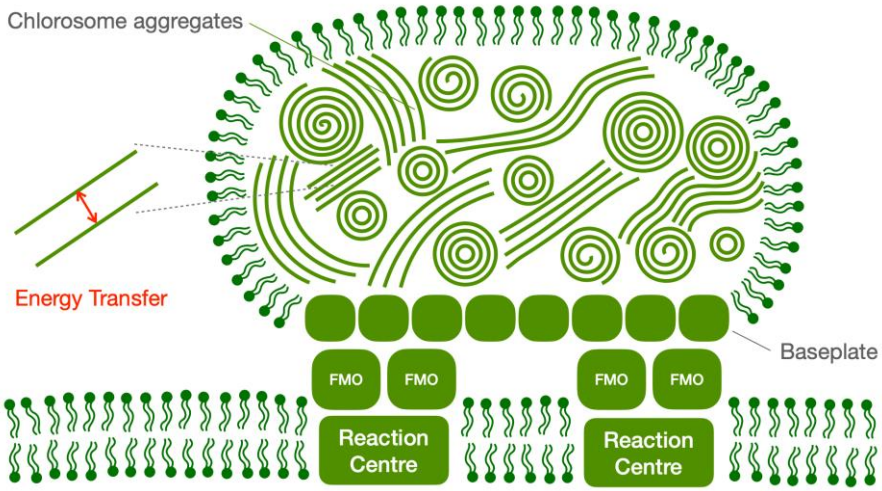
Chlorosome Lamella

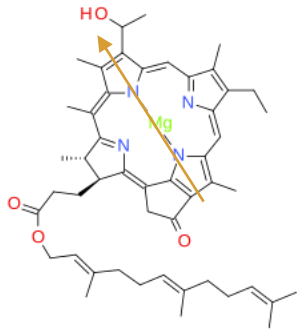


- Chlorosomes are the most efficient light harvesting antenna we know.
- Arrangements of thousands of closely packed BChl *c* molecules.
- Two-dimensional structures.
- Little is known about the lamella structures and transfer between them.

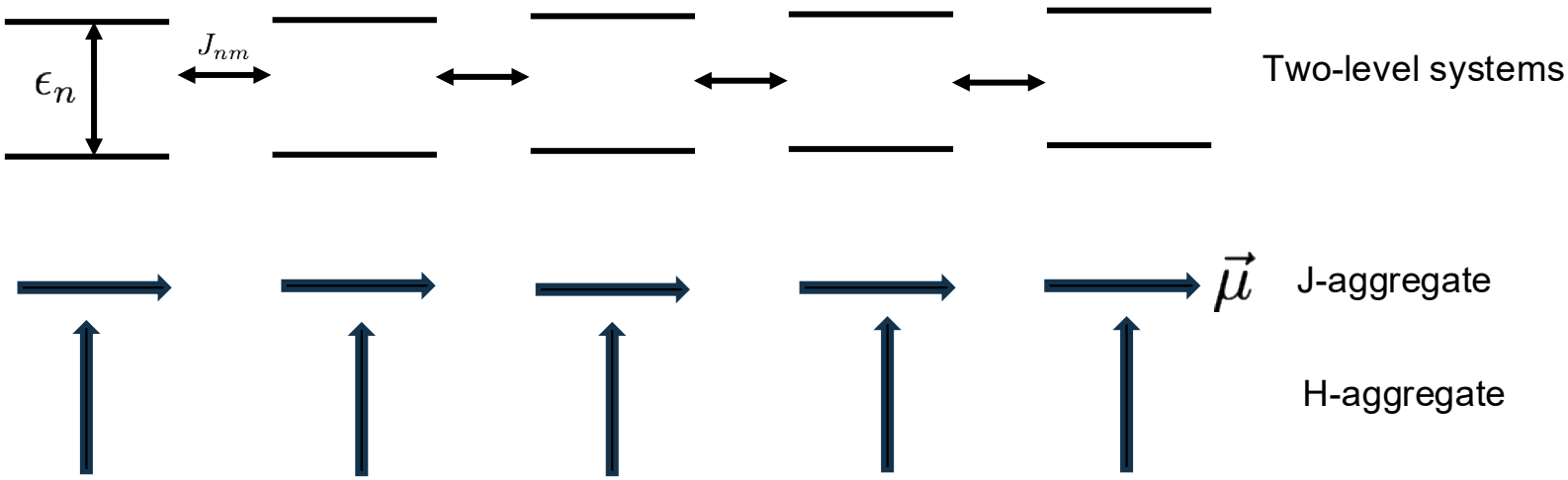
J. Phys. Chem. Lett. **16**:12507 (2025)

Frenkel Exciton Model

BChl *c*



$$H = \sum_n \epsilon_n B_n^\dagger B_n + \sum_{m \neq n} J_{nm} B_n^\dagger B_m$$



Numerical Integration of the Schrödinger Equation (NISE)

- Neglects feedback to bath!
- Allows using precalculated trajectories.
- Can be scaled to very large systems
- Thermalize to ‘infinite’ temperature.

Time-dependent Schrödinger Equation:

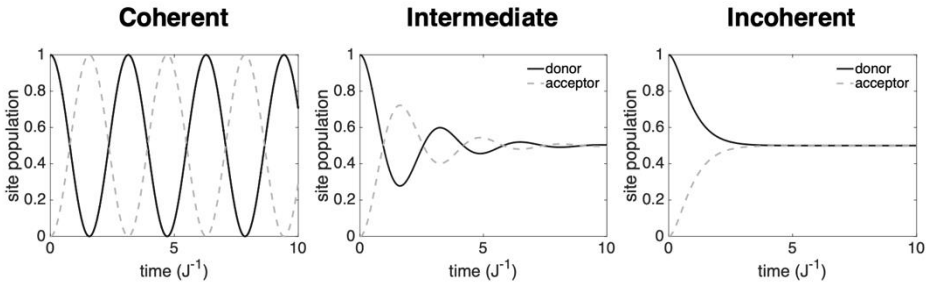
$$\frac{d\phi(t)}{dt} = -\frac{i}{\hbar}H(t)\phi(t)$$

Time-evolution operator:

$$U(m\Delta t, 0) = T\prod_{n=0}^{m-1}\exp\left(-\frac{i}{\hbar}H(n\Delta t)\Delta t\right)$$

DOI: 10.1021/jp064795t

Population Transfer



- Donor to acceptor transfer

Time-dependent Schrödinger Equation:

$$\frac{d\phi(t)}{dt} = -\frac{i}{\hbar}H(t)\phi(t)$$

Time-evolution operator:

$$U(m\Delta t, 0) = T\prod_{n=0}^{m-1}\exp\left(-\frac{i}{\hbar}H(n\Delta t)\Delta t\right)$$

Population on acceptor:

$$P_A(t) = \langle\langle A|U(t,0)|D\rangle\langle D|U(0,t)|A\rangle\rangle_E$$

Rates can be obtained by fitting to a kinetic model in the incoherent limit
J. Phys. Chem. B 110:22910-22916 (2006), 10.1016/j.chemphys.2019.110478

Fermi's Golden Rule

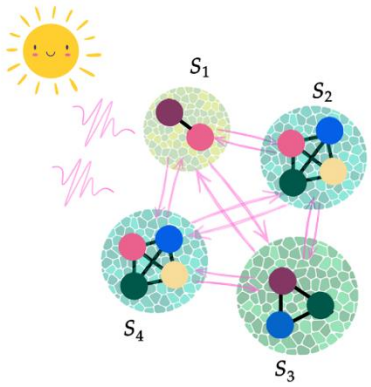
- Rates for physical processes often conveniently described using second-order perturbation theory resulting in Fermi's golden rule expressions:

$$k_{fi} = \frac{2\pi}{\hbar} |\langle \phi_f | V | \phi_i \rangle|^2 \rho(E_f - E_i)$$

- Enrico Fermi called this "golden rule No. 2", but it was first derived by Paul Dirac.

Dirac, P. A. M. "The Quantum Theory of Emission and Absorption of Radiation". Proceedings of the Royal Society A. 114: 243–265 (1927)

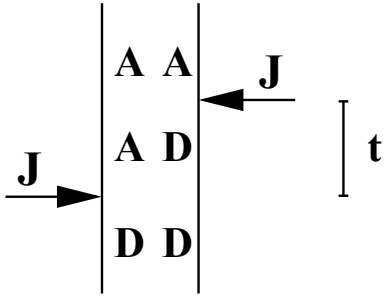
Time-domain Multichromophoric FRET



- From 2nd order perturbation theory

$$k = \frac{2\mathrm{Re}}{\hbar^2} \int_0^\infty dt\ \mathrm{Tr}[J^{\mathrm{A}D} E^{\mathrm{D}}(t) J^{\mathrm{D}A} I^{\mathrm{A}}(t)]$$

$\frac{J^2}{\Gamma_{AB}}$



$$I^{\mathrm{A}}_{\mathrm{d}b}(t) = \left\langle \langle A_{\mathrm{d}} | U_0(t,0) | A_{\mathrm{b}} \rangle \right\rangle$$

$$E^{\mathrm{D}}_{\mathrm{ac}}(t) = \left\langle \langle D_{\mathrm{a}} | \rho(0) U_0(0,t) | D_{\mathrm{c}} \rangle \right\rangle$$

Higher order terms require more interactions
- Longer time needed – SLOWER!

K. Zhong *et al*. J.Chem.Phys. 158:064103 (2023)

Ma, Cao, J. Chem. Phys. 142:094106 (2015)
Sumi J. Phys. Chem. B 103:252 (1999)

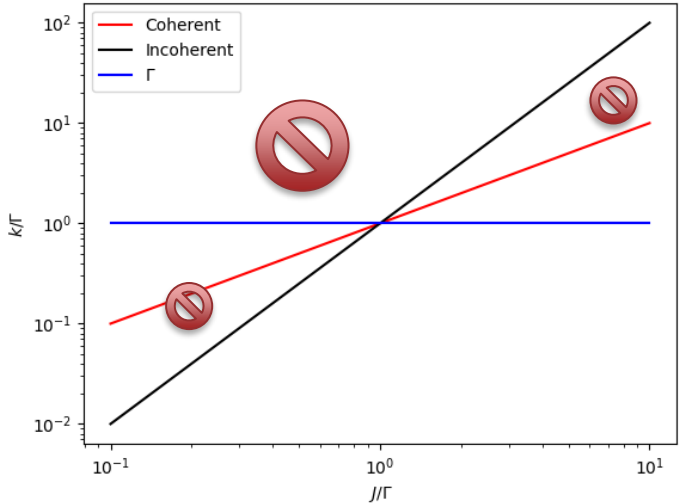
Speed limit of transfer

- Ultimate limit – Coherent

$$k < \frac{2J}{\hbar}$$

- Incoherent limit

$$k \leq \frac{2J^2}{\Gamma_{AB}\hbar^2} \qquad (k \gg \Gamma_{AD})$$



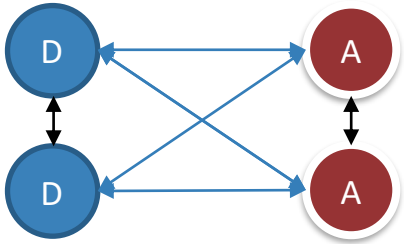
If $k > 2J$ or Γ_{AB} MC-FRET is not valid!

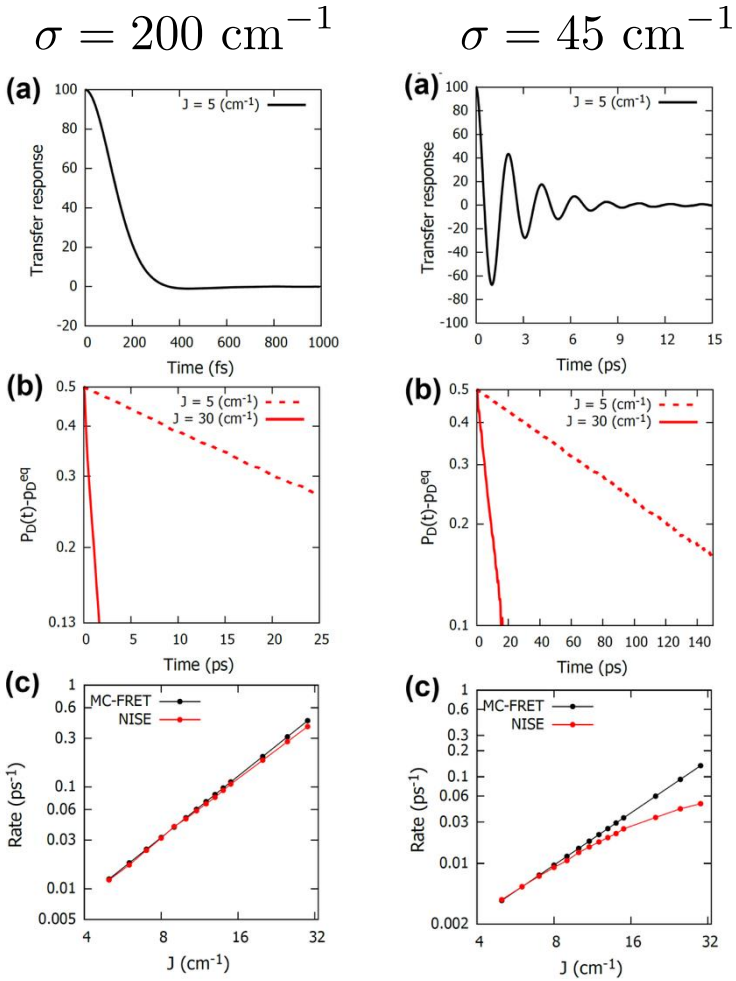
Coherent / “quantum” when $J, k > \Gamma_{AD}$

K. Zhong *et al*. J.Chem.Phys. 158:064103 (2023)

Examples

- Transfer between two dimers

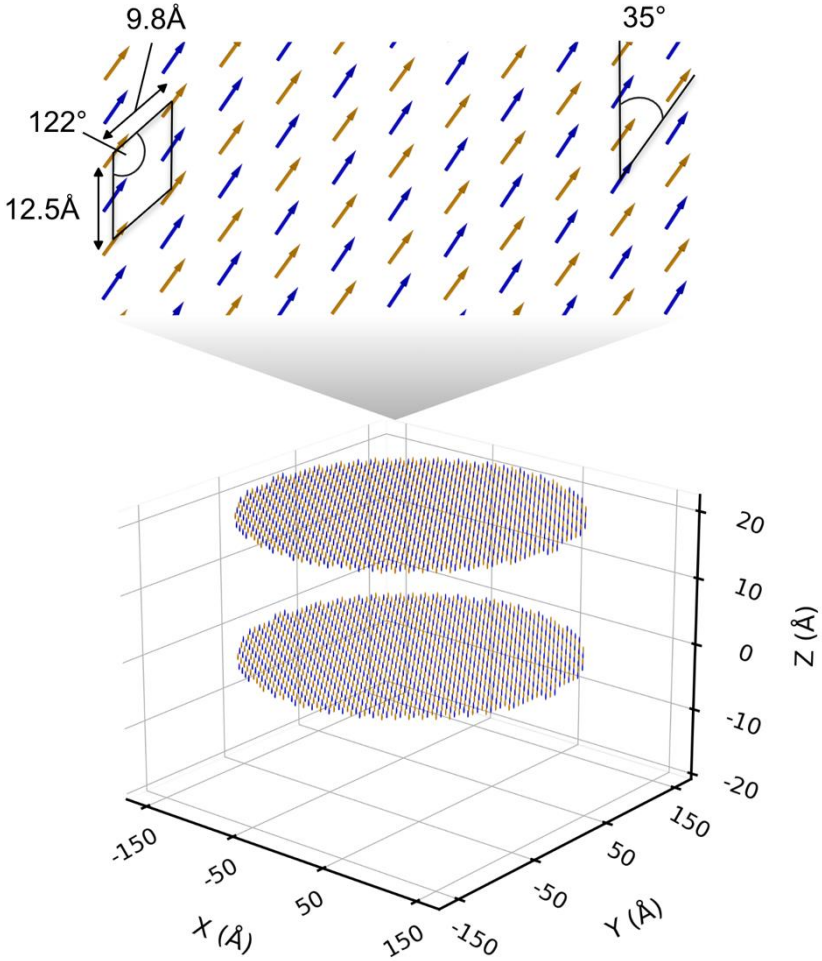




K. Zhong *et al*. J.Chem.Phys. 158:064103 (2023)

Chlorosome Lamella

- In stacked graphene the angle between sheets is crucial and even leads to superconductivity at 1.5° stacking angle. Does the angle affect the energy transfer between chlorosome lamella?



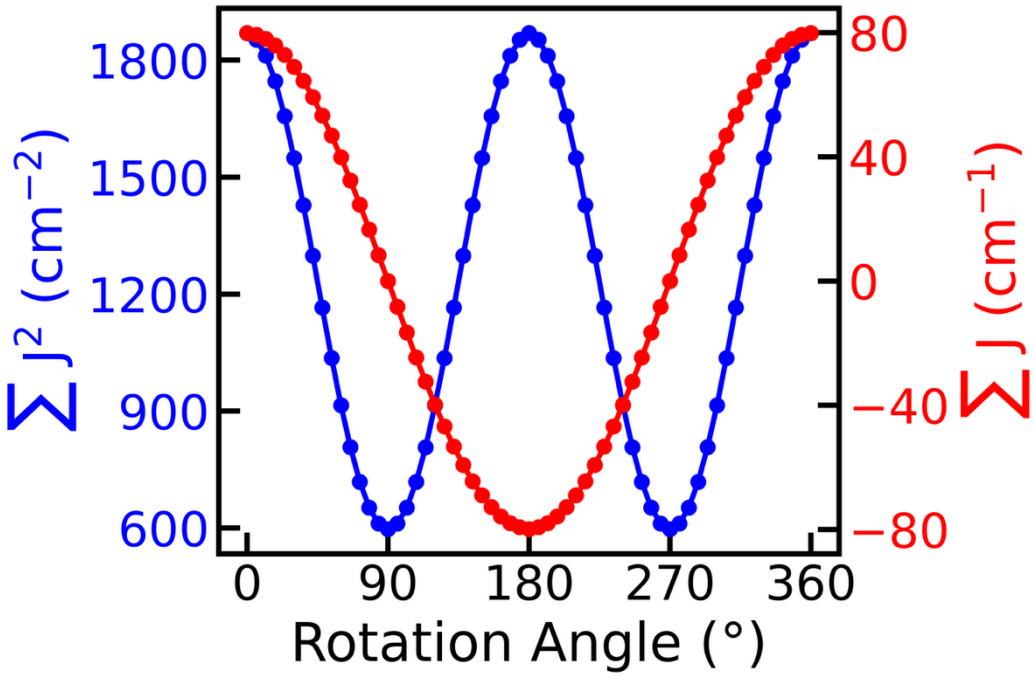
Sheet parameters from NMR: Proc. Nat. Acad. Sci. 106:8525 (2009)

Chlorosome Lamella

- Trivial effect from rotating dipoles.

Expectation for transfer between Individual chromophores:

$$k \leq \frac{2J^2}{\Gamma_{AB}\hbar^2}$$



$$J_{nm} = \frac{1}{4\pi\epsilon_0} \frac{\vec{\mu}_n \cdot \vec{\mu}_m - 3(\vec{\mu}_n \cdot \vec{u}_{nm})(\vec{u}_{nm} \cdot \vec{\mu}_m)}{r_{nm}^3}$$

We used the transition-dipole approximation.
Transition-dipole is 5.48 Debye

Chlorosome Lamella

Xinmeng Li
(U. Leiden)

Vesna Erić
(MPI Mainz)

- Frequency fluctuations
  - Molecular Dynamics on Tubes (OPLS with GROMACS)
  - Electrostatic Mapping (Renger Style)
  - We assume fluctuations similar to those in the tubes
  - Two overdamped Brownian oscillators

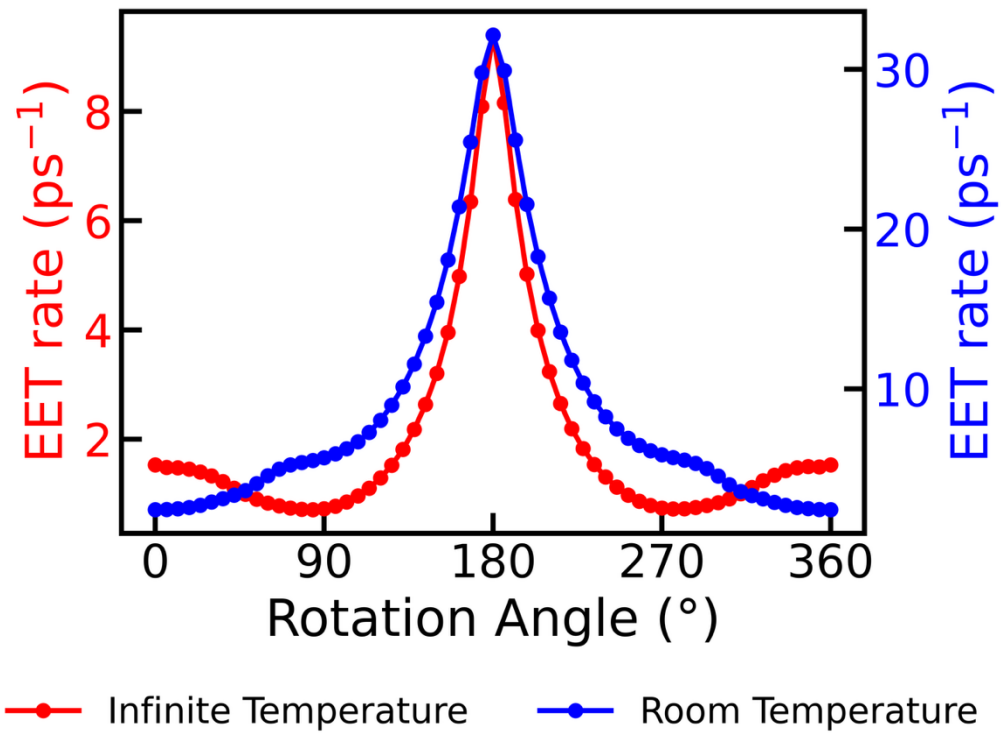
230 cm^{-1} and 1.2 ps
185 cm^{-1} and 50 fs

$$\Delta\omega_n(t) = \frac{1}{4\pi\varepsilon_0}\sum_{m}^{M}\sum_{l\neq m}^{L}\frac{(q_m^e - q_m^g)q_l^g}{R_{ml}(t)}$$

Electrostatic Mapping: Photosynth. Res. 95:97−209 (2008)
Quantum-Classical Simulations: J. Phys. Chem. B 127:1097 (2023)
Noise generation: Chem. Phys. 529:110478 (2020)

Chlorosome Lamella

- Transfer calculated using the TD-MCFRET approach.
- Enhanced transfer at 180° and suppressed at 0°!

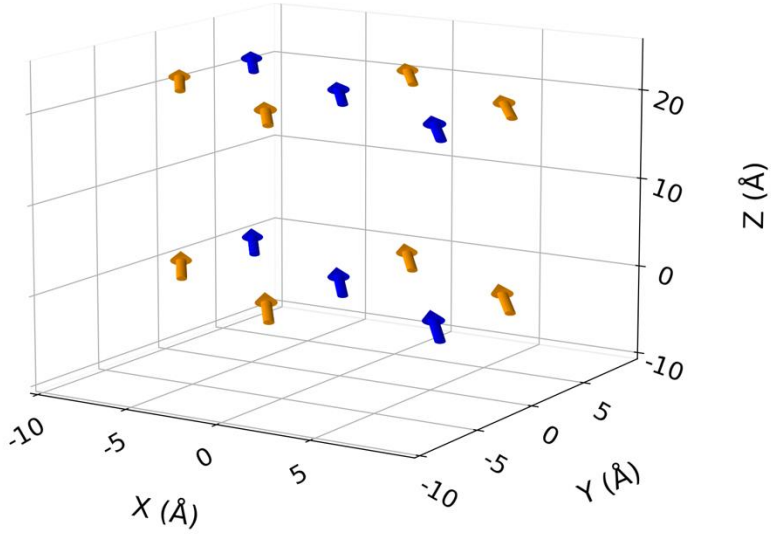


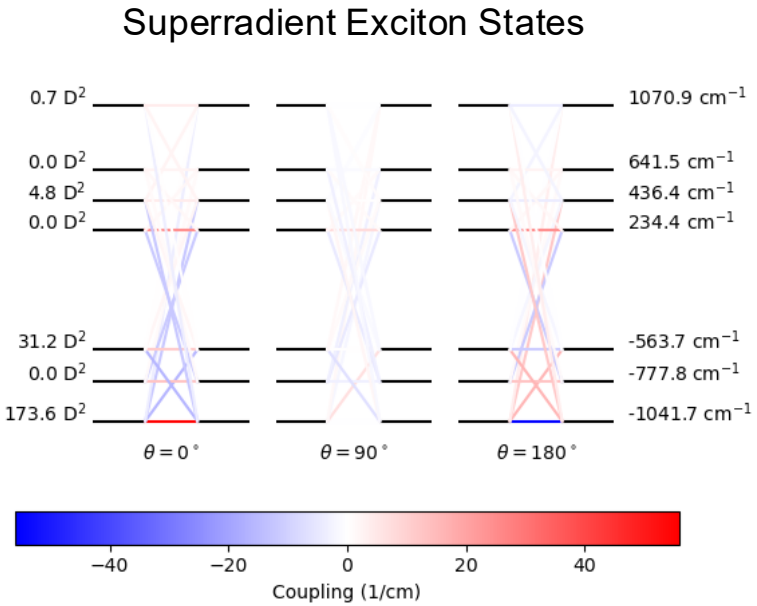
Initial State:

$$\rho(0) = \frac{\exp(-H(0)/k_B T)}{\mathrm{Tr}(\exp(-\mathrm{H}(0)/\mathrm{k_B T}))}$$

Chlorosome Lamella

- Model system shows the coupling pattern





Transfer between dark states due to delocalization

Chlorosome Lamella Summary

- We expect a large speedup in exciton transfer between clorosome lamella if oriented in an anti-parallel arrangement.
- Similar effect can be expected for transfer between other two-dimensional materials.
- We currently investigate effects on transfer between tubes.

See also: ten Hoven et al. J. Chem. Phys. 164:014115 (2026)

Speed up of Quantum Processes

Roel Tempelaar
Northwestern University

THE JOURNAL OF PHYSICAL CHEMISTRY Letters
Letter
pubs.acs.org/JPCL

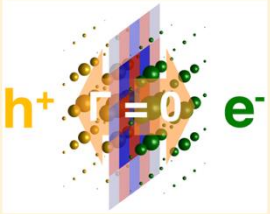
Charge Recombination Suppressed by Destructive Quantum Interference in Heterojunction Materials

Roel Tempelaar,[†] L. Jan Anton Koster,[†] Remco W. A. Havenith,[†,‡,§] Jasper Knoester,[†] and Thomas L. C. Jansen*[,†]

[†]Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
[‡]Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands
[§]Ghent Quantum Chemistry Group, Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 (S3), B-9000 Gent, Belgium

Supporting Information

ABSTRACT: We show that charge recombination in ordered heterojunctions depends sensitively on the degree of coherent delocalization of charges at the donor–acceptor interface. Depending on the relative sign of the electron and hole transfer integrals, such delocalization can dramatically suppress recombination through destructive quantum interference. This could explain why measured recombination rates are significantly lower than predictions based on Langevin theory for a variety of organic bulk heterojunctions. Moreover, it opens up a design strategy for photovoltaic devices with enhanced efficiencies through coherently suppressed charge recombination.



THE JOURNAL OF PHYSICAL CHEMISTRY Letters
ACS AuthorChoice
Letter
Cite This: J. Phys. Chem. Lett. 2017, 8, 6113–6117
pubs.acs.org/JPCL

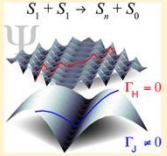
Exciton–Exciton Annihilation Is Coherently Suppressed in H-Aggregates, but Not in J-Aggregates

Roel Tempelaar,*[,†,‡] Thomas L. C. Jansen,[†] and Jasper Knoester*[,†]

[†]Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
[‡]Department of Chemistry, Columbia University, 3000 Broadway, New York, New York 10027, United States

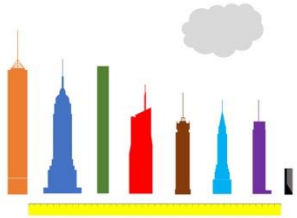
Supporting Information

ABSTRACT: We theoretically demonstrate a strong dependence of the annihilation rate between (singlet) excitons on the *sign* of dipole–dipole couplings between molecules. For molecular H-aggregates, where this sign is positive, the phase relation of the delocalized two-exciton wave functions causes a destructive interference in the annihilation probability. For J-aggregates, where this sign is negative, the interference is constructive instead; as a result, no such coherent suppression of the annihilation rate occurs. As a consequence, room temperature annihilation rates of typical H- and J-aggregates differ by a factor of ~3, while an order of magnitude difference is found for low-temperature aggregates with a low degree of disorder. These findings, which explain experimental observations, reveal a fundamental principle underlying exciton–exciton annihilation, with major implications for technological devices and experimental studies involving high excitation densities.



Tempelaar *et al.* J. Chem. Lett. 7:198 (2016) and J. Chem. Lett. 8:6113 (2017)

The Manhattan Exciton Size

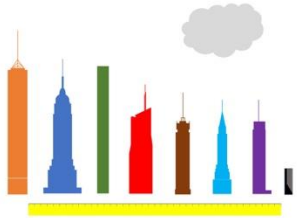


- Is there an easy way to predict the maximal speedup due to constructive quantum interference?

$$k = \frac{2\pi}{\hbar} |\sum_n c_{kn}|^2 |\vec{\mu_n}|^2 \rho(E_k - E)$$

$$|\phi_k\rangle = \sum_n c_{kn} |\psi_n\rangle$$

The Manhattan Exciton Size



Motivated by connecting delocalization more directly with superradiance.

$$\vec{\mu}_k = \sum_m c_{km}\vec{\mu}_m. \qquad |\vec{\mu}_k| = \sum_m |c_{km}||\vec{\mu}|$$

$$N^*_{IPR,k} = \left(\sum_m |c_{km}|^4\right)^{-1}$$

$$N^*_{MES,k} = \left(\sum_m |c_{km}|\right)^2$$

$$\mathcal{I}_k = |\vec{\mu}_k|^2 = \left(\sum_m |c_{km}|\right)^2 |\vec{\mu}|^2$$

$$\mathcal{I}_k = N^*_{MES,k}|\vec{\mu}|^2$$

$$\frac{1}{N}\sum_k \langle N^*_{MES,k}\rangle = \frac{1}{N}\sum_{n,m} \rho^{ADM}_{nm}$$

Phys. Rep. 13, 93 (1974); J. Phys. Chem. B 105, 5515 (2001)

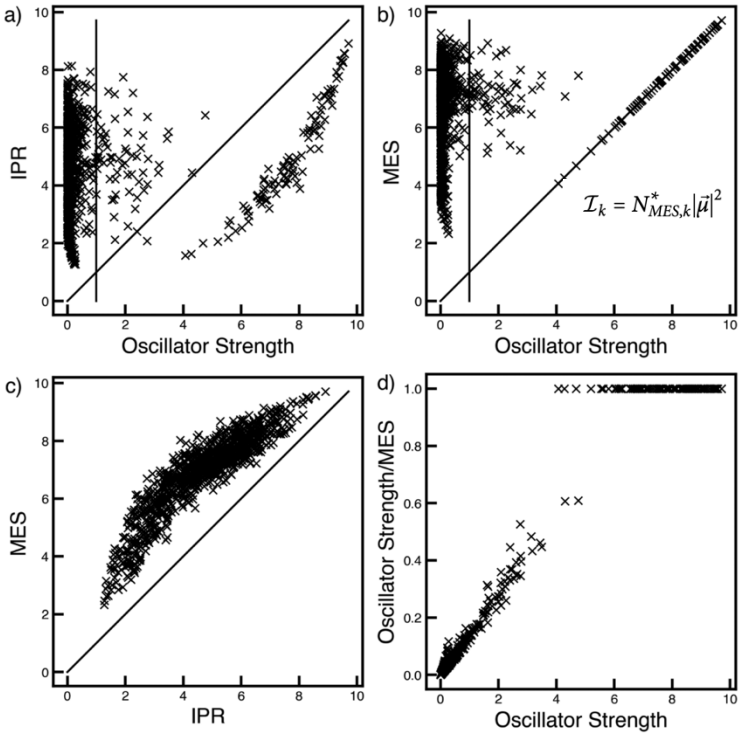
J. Chem. Phys. 162, 074113 (2025)

The Manhattan Exciton Size

Strong connection with intensity of superradient states.

$$N^*_{IPR,k} = \left(\sum_m |c_{km}|^4 \right)^{-1}$$

$$N^*_{MES,k} = \left(\sum_m |c_{km}| \right)^2$$



Phys. Rep. 13, 93 (1974); J. Phys. Chem. B 105, 5515 (2001)

J. Chem. Phys. 162, 074113 (2025)

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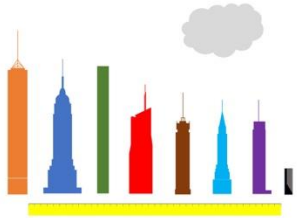


- In summary: The MES provides an upper limit for the enhancement of the speedup due to quantum interference. (Assuming second order perturbation theory.)
  At the same time a meassure for exciton delocalization.

$$N^{*}_{MES,k} = \left(\sum_{m} |c_{km}| \right)^{2}$$

$$k = \frac{2\pi}{\hbar} \left| \sum_{n} c_{kn} \right|^{2} |\vec{\mu_n}|^{2} \rho(E_k - E)$$

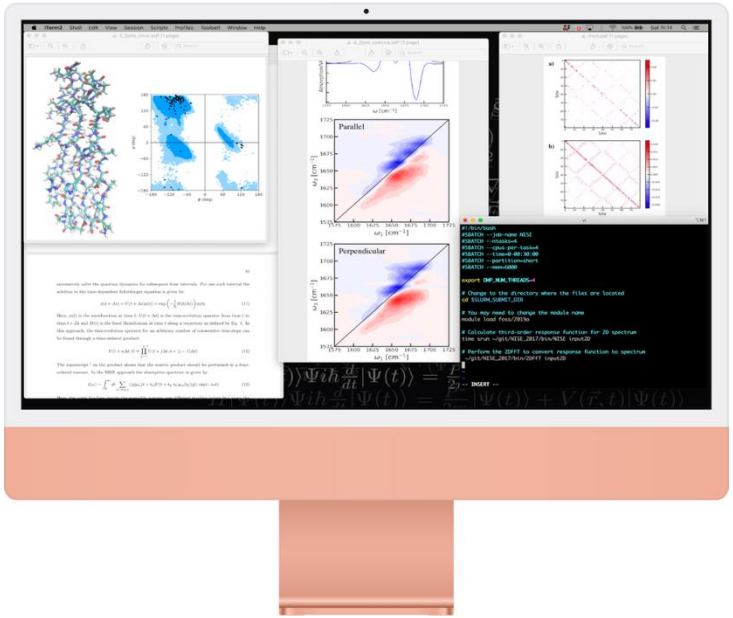
$$\left(\sum_{m} |c_{km}| \right)^{2} \geq \left| \sum_{m} c_{km} \right|^{2}$$

J. Chem. Phys. 162, 074113 (2025)

Conclusions

- Quantum Interference demonstrated for
  - Exciton transfer in biological systems
- Open Questions
  - Can we detect the twist angle in the Chlorosomes?
  - Did the Green Sulphur Bacteria evolve to use the interference for speeding up exciton transfer?
  - How large is the effect in other two-dimensional materials?

Numerical Integration of the Schrödinger Equation



GHlacour / NISE_2017 Public

Watch 0

Code | Issues 1 | Pull requests | Actions | Projects | Wiki

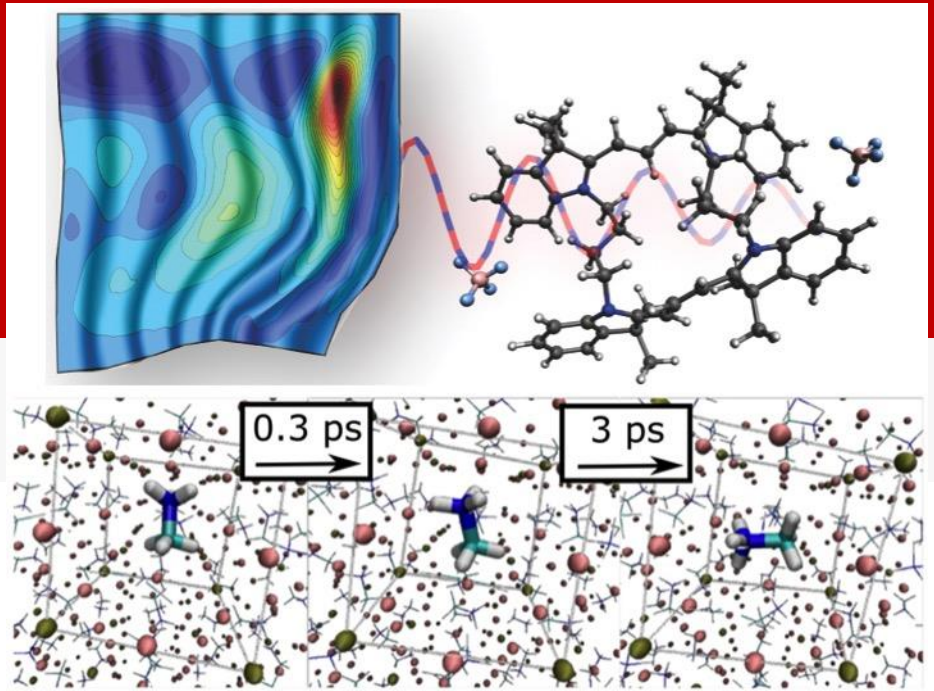
master | 10 branches | 0 tags | Go to file | Add file | Code

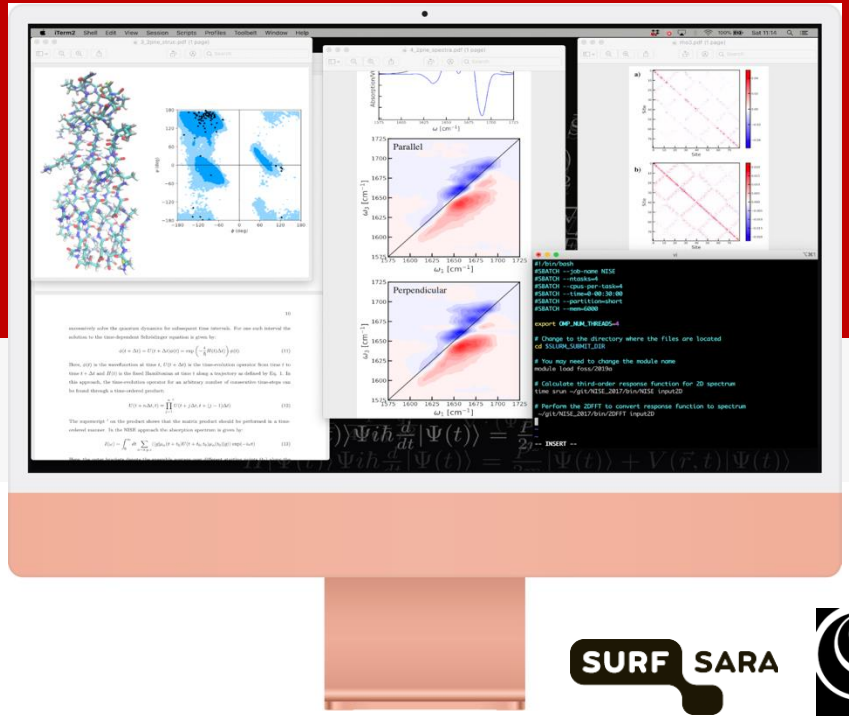
GHlacour Merge pull request #23 from GHlaco... af09b6c on 31 Oct 157 commits

.github/ISSUE_TEMPL...	Removed the smartphone options	15 months ago
cmake	Further changes to build system	3 years ago
doc	Made updates in the documentation including ad...	3 months ago
example	Changed the 2DFFT program so non-existing po...	8 months ago
src	Removed obsolete version of absorption calculat...	2 months ago
.gitattributes	Cleaned up repository, added CMake	3 years ago
.gitignore	Further changes to build system	3 years ago
CMakeLists.txt	Refactored a lot, introduced 2D arrays among ot...	3 years ago
CONTRIBUTING.md	Create CONTRIBUTING.md	3 years ago

- https://github.com/GHlacour/NISE_2017

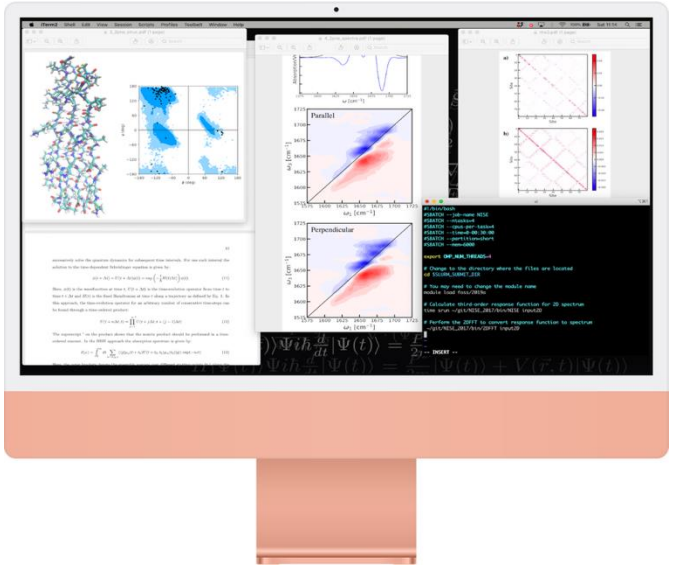
Thank you!





Financial Support

PhotoCAM – Marie Curie Doctoral Network



Fermi's Golden Rule

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$$k_{fi} = \frac{2\pi}{\hbar} |\langle \phi_f | V | \phi_i \rangle|^2 \rho(E_f - E_i)$$

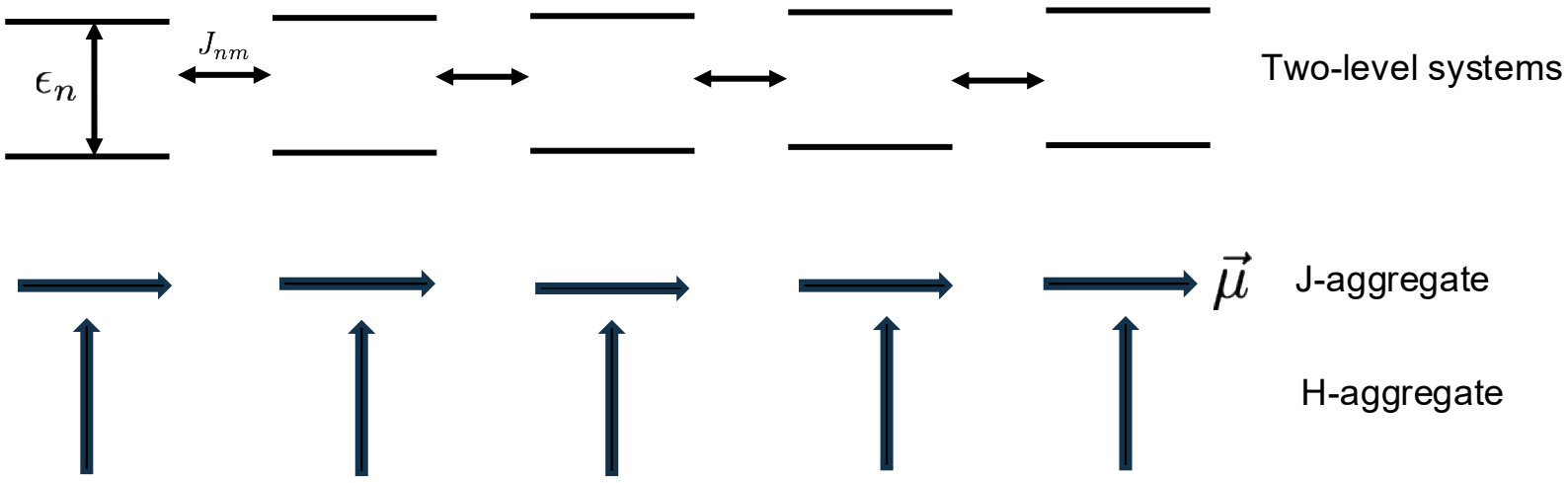
- Enrico Fermi called this "golden rule No. 2", but it was first derived by Paul Dirac.

Dirac, P. A. M. "The Quantum Theory of Emission and Absorption of Radiation". Proceedings of the Royal Society A. 114: 243–265 (1927)

Superradiance

- Frenkel Exciton Model

$$H = \sum_n \epsilon_n B_n^\dagger B_n + \sum_{m \neq n} J_{nm} B_n^\dagger B_m$$



Superradiance

- A well-known realization of quantum interference.

$$H = \sum_n \epsilon_n B_n^\dagger B_n + \sum_{m \neq n} J_{nm} B_n^\dagger B_m$$

Specific eigenstate:

$$|\phi_k\rangle = \sum_n c_{kn} |n\rangle$$

Assuming linear aggregate:

$$\langle g|\mu|n\rangle = \vec{\mu}_n = \vec{\mu}$$

$$k = \frac{2\pi}{\hbar} |\langle \phi_k|\mu|g\rangle|^2 \rho(E_k - E_g) = \frac{2\pi}{\hbar} |\sum_n c_{kn} \langle n|\mu|g\rangle|^2 \rho(E_k - E_g)$$

$$k = \frac{2\pi}{\hbar} |\sum_n c_{kn}|^2 |\vec{\mu}|^2 \rho(E_k - E_g)$$

Dicke, Robert H. "Coherence in Spontaneous Radiation Processes". Physical Review. 93: 99–110 (1954)

Superradiance

$$k = \frac{2\pi}{\hbar} |\sum_n c_{kn}|^2 |\vec{\mu}|^2 \rho(E_k - E_g)$$

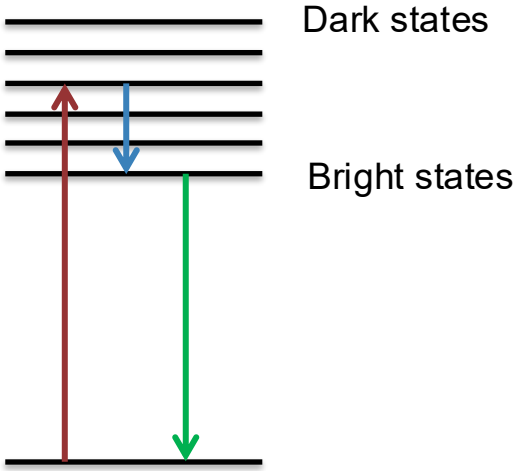
- Constructive interference for states with all positive wave function coefficients. Leading to superradiance. Perfect delocalization over N sites leads to N times stronger transition than for an isolated molecule.

$$|\sum_n c_{kn}|^2 = |\sum_n \frac{1}{\sqrt{N}}|^2 = N \qquad \sum_n |c_{kn}|^2 = 1$$

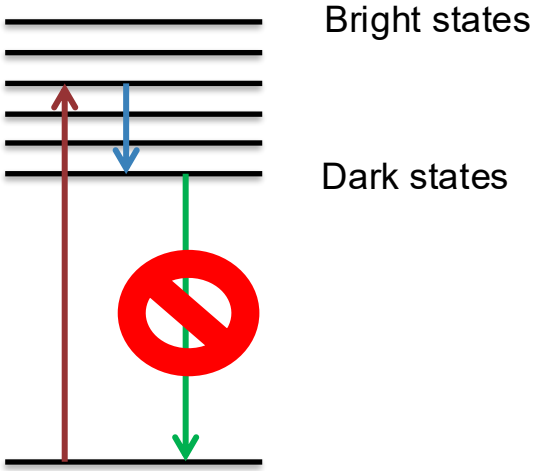
- Destructive interference for states with a mix of positive and negative coefficients. Leading to dark states.

Superradiance

J-aggregate
Lowest state is superradiant
Strong fluorescence



H-aggregate
Lowest state has no oscillator strength
Weak or no fluorescence



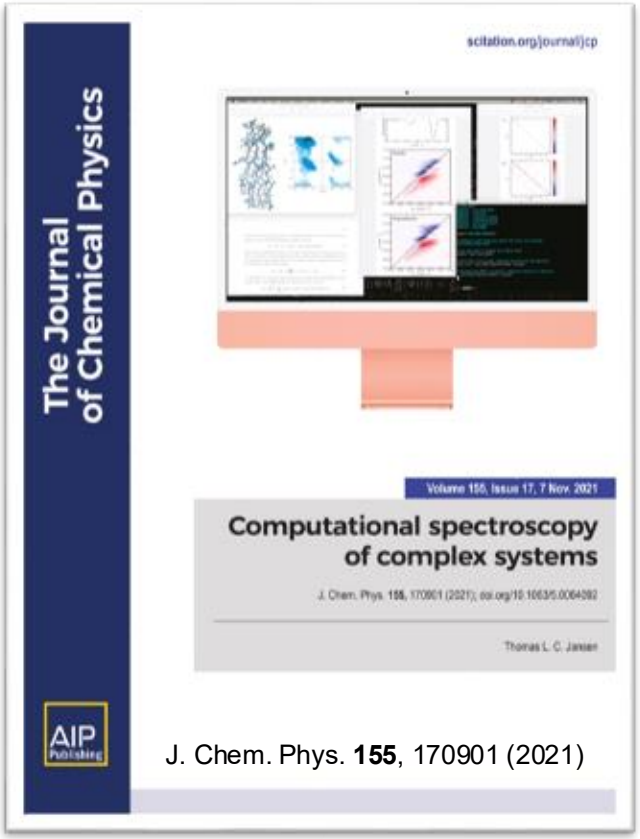
Superradiance

In summary:

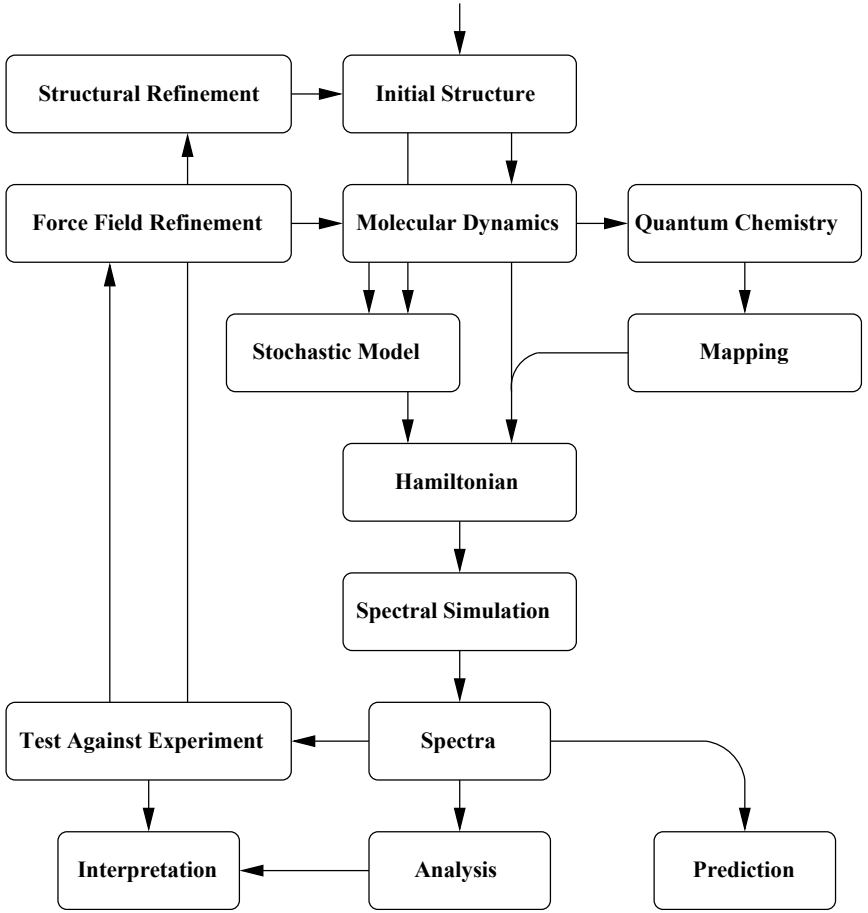
- Delocalization of the wavefunction leads to superradiant states carying most of the oscillator strength and to dark states, which do not emit light.

Sum rule: It turns out that the sum over all oscillator strenghts is conserved. So overall the absorption cross section does not change. However, for fluorescence only the lowest energy states matters.

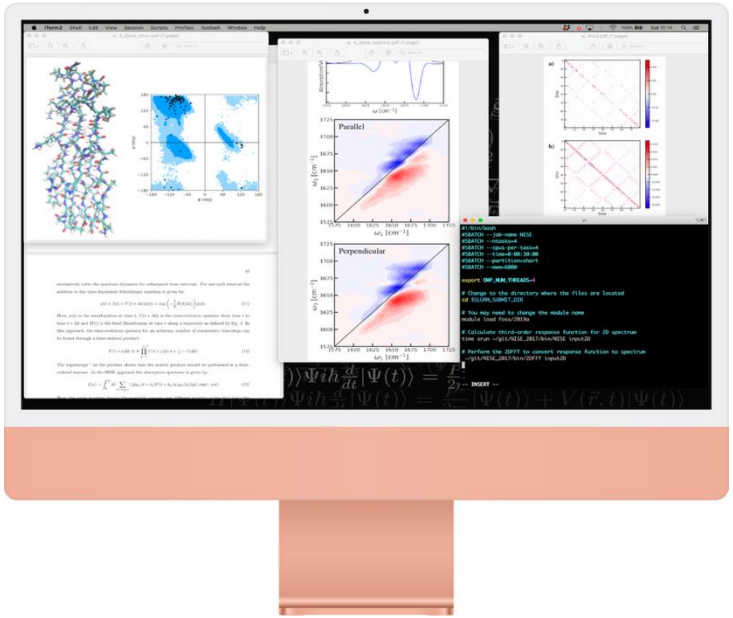
Computational Spectroscopy Methodology



J. Chem. Phys. **155**, 170901 (2021)



Numerical Integration of the Schrödinger Equation



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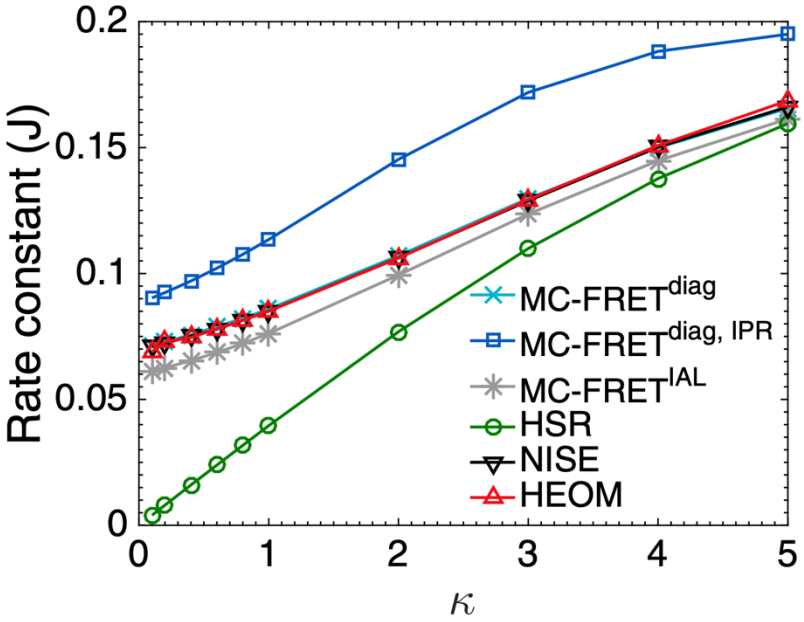
GHlacour Merge pull request #23 from GHlaco... af09b6c on 31 Oct 157 commits

.github/ISSUE_TEMPL...	Removed the smartphone options	15 months ago
cmake	Further changes to build system	3 years ago
doc	Made updates in the documentation including ad...	3 months ago
example	Changed the 2DFFT program so non-existing po...	8 months ago
src	Removed obsolete version of absorption calculat...	2 months ago
.gitattributes	Cleaned up repository, added CMake	3 years ago
.gitignore	Further changes to build system	3 years ago
CMakeLists.txt	Refactored a lot, introduced 2D arrays among ot...	3 years ago
CONTRIBUTING.md	Create CONTRIBUTING.md	3 years ago

- https://github.com/GHlacour/NISE_2017

Benchmarking MC-FRET



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Comparison of methods to study excitation energy transfer in molecular multichromophoric systems

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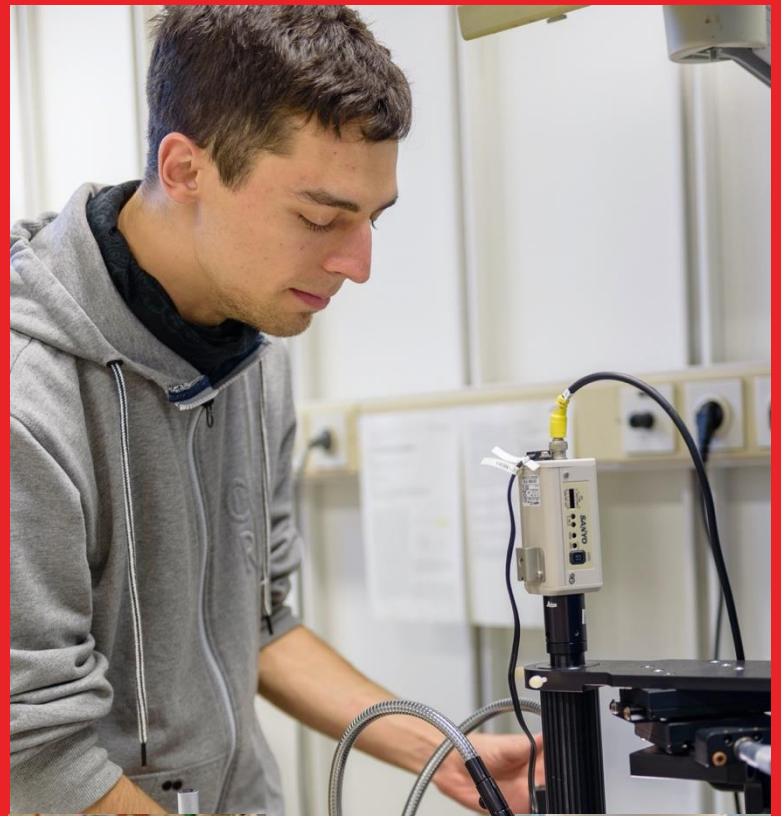

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