Electron and energy transfer dynamics in light harvesting systems

Thomas P. Fay & David Limmer
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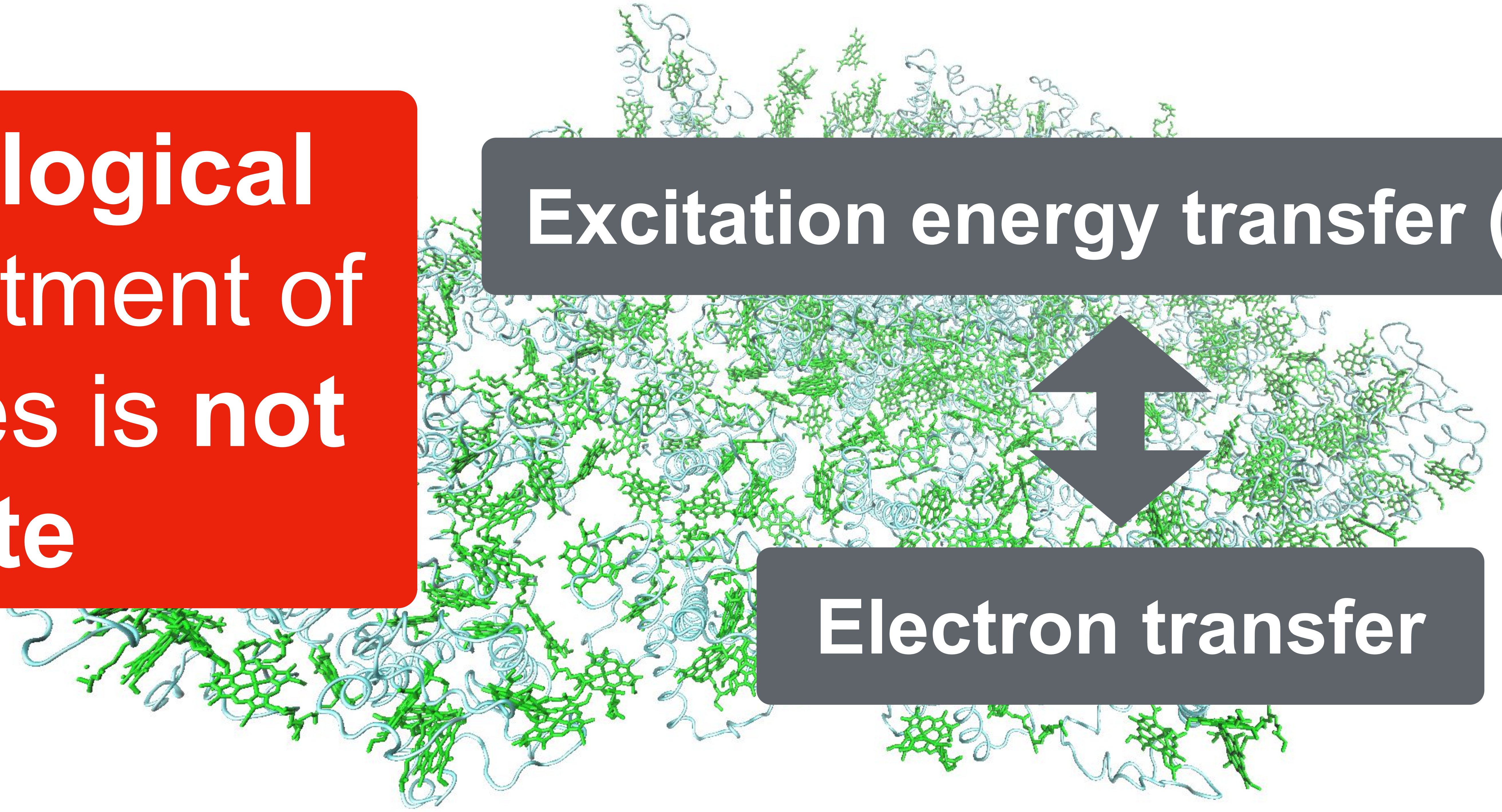
Electron transfer in photosynthesis

Electron transfer in photosynthesis

→

Photoprotection
(non-photochemical quenching **NPQ**)

Phenomenological Lindblad treatment of loss processes is **not accurate**



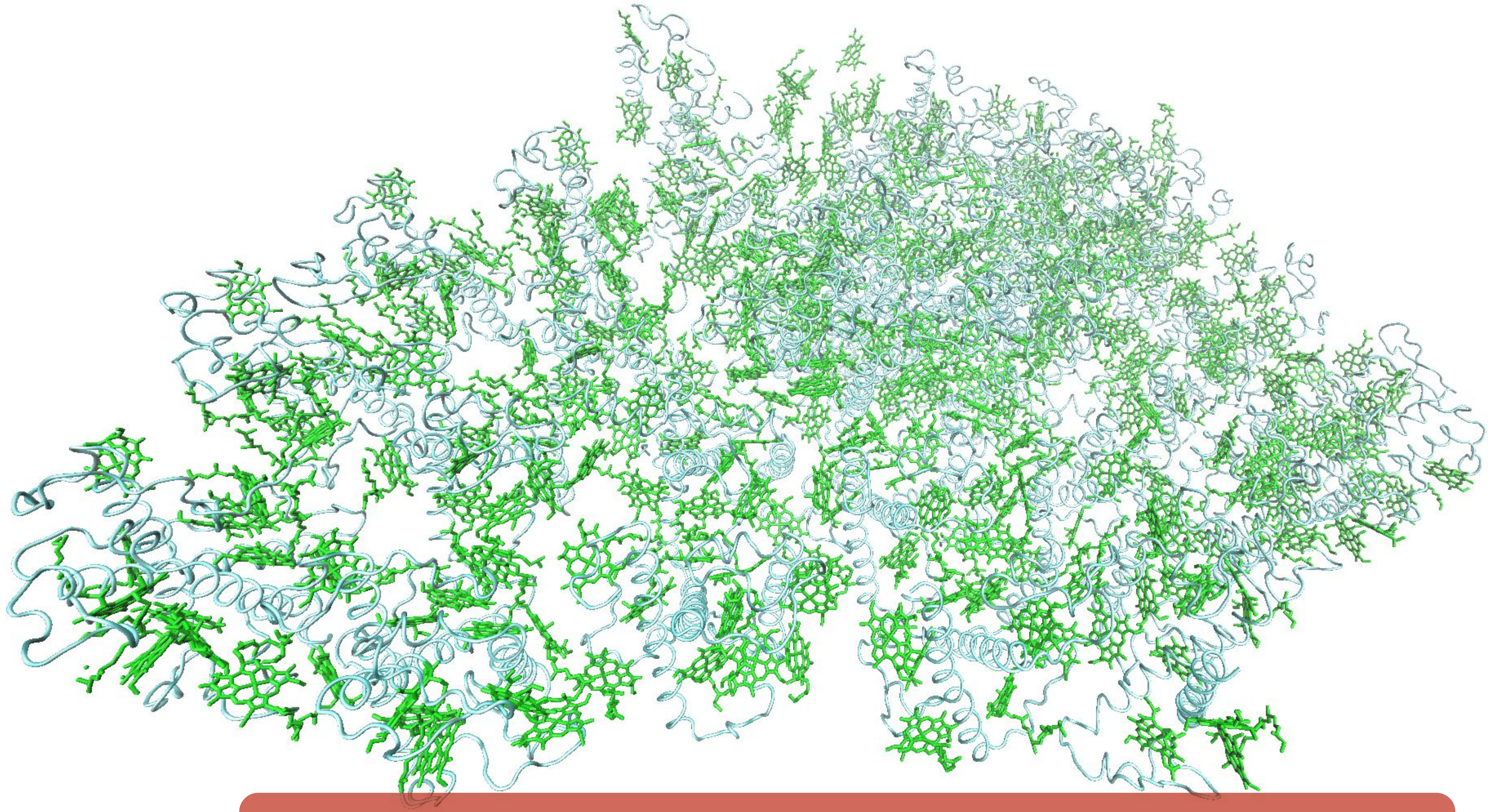
Excitation energy transfer (EET)

↕

Electron transfer

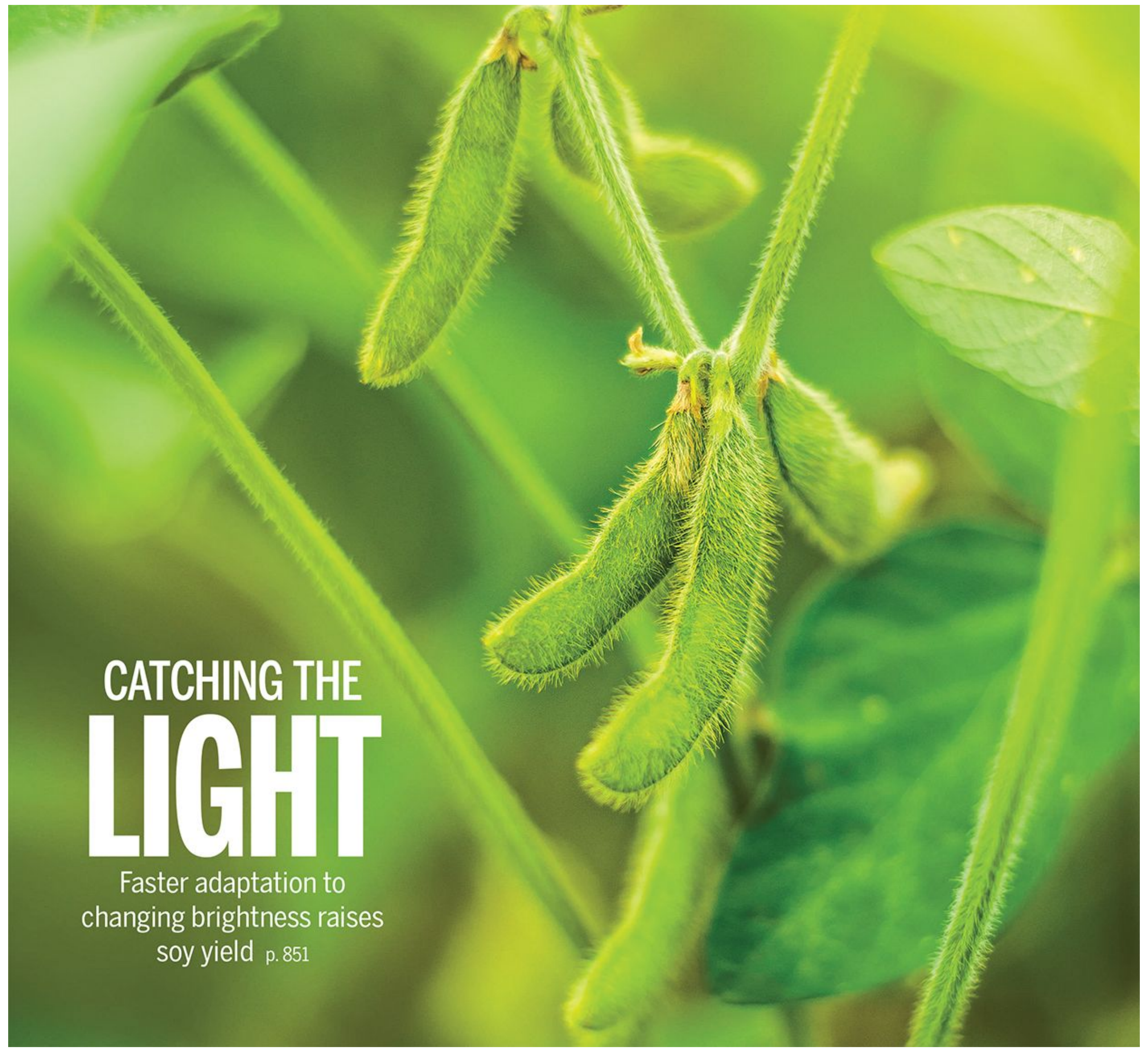
Photoprotection is essential for life

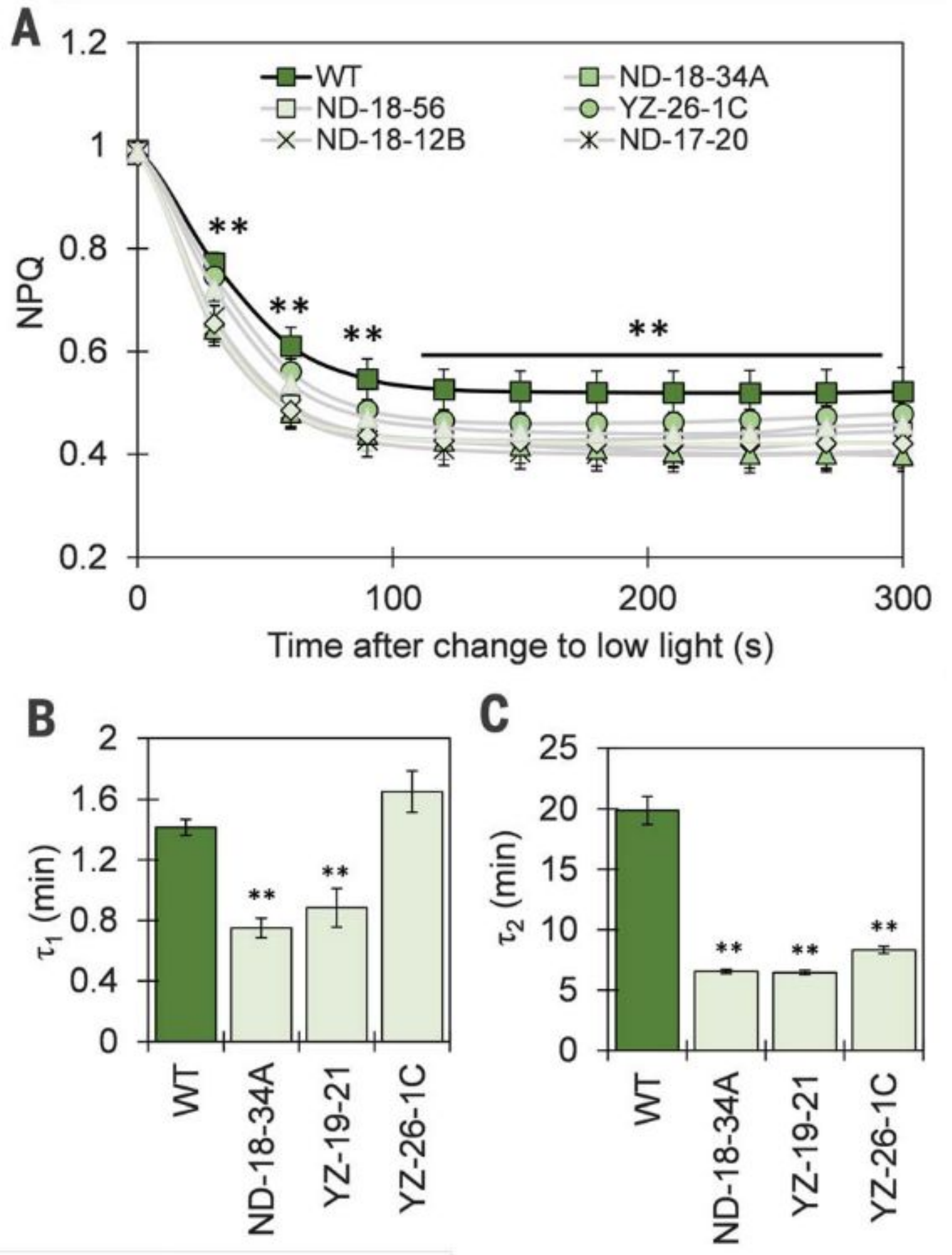
Fluctuating light sources → Excess light **damages** organisms → Real-time adaptive **non-photochemical quenching (NPQ)**



Photoprotection controls crop yields

Modification of NPQ related genes → 30% higher crop yields

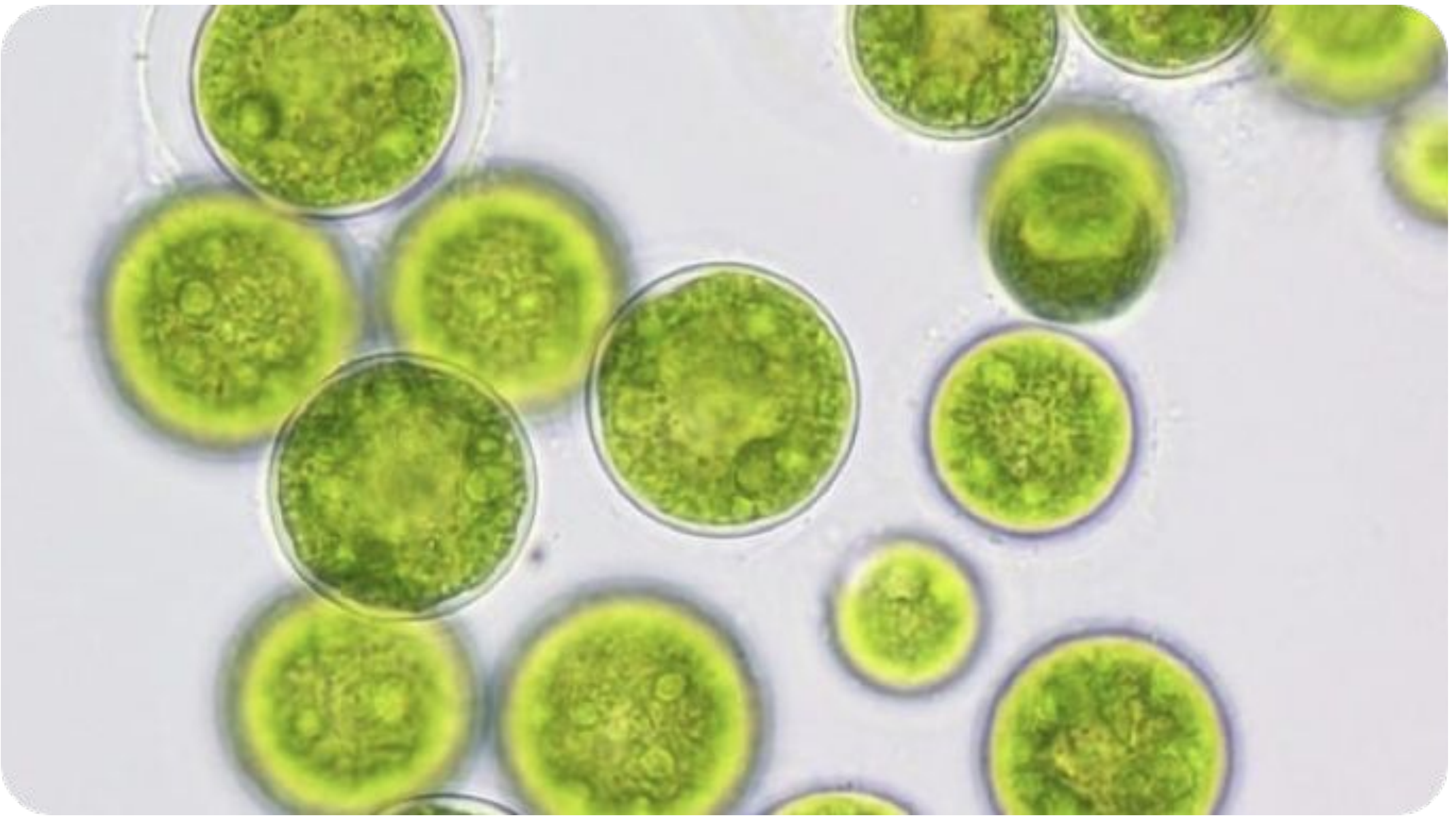




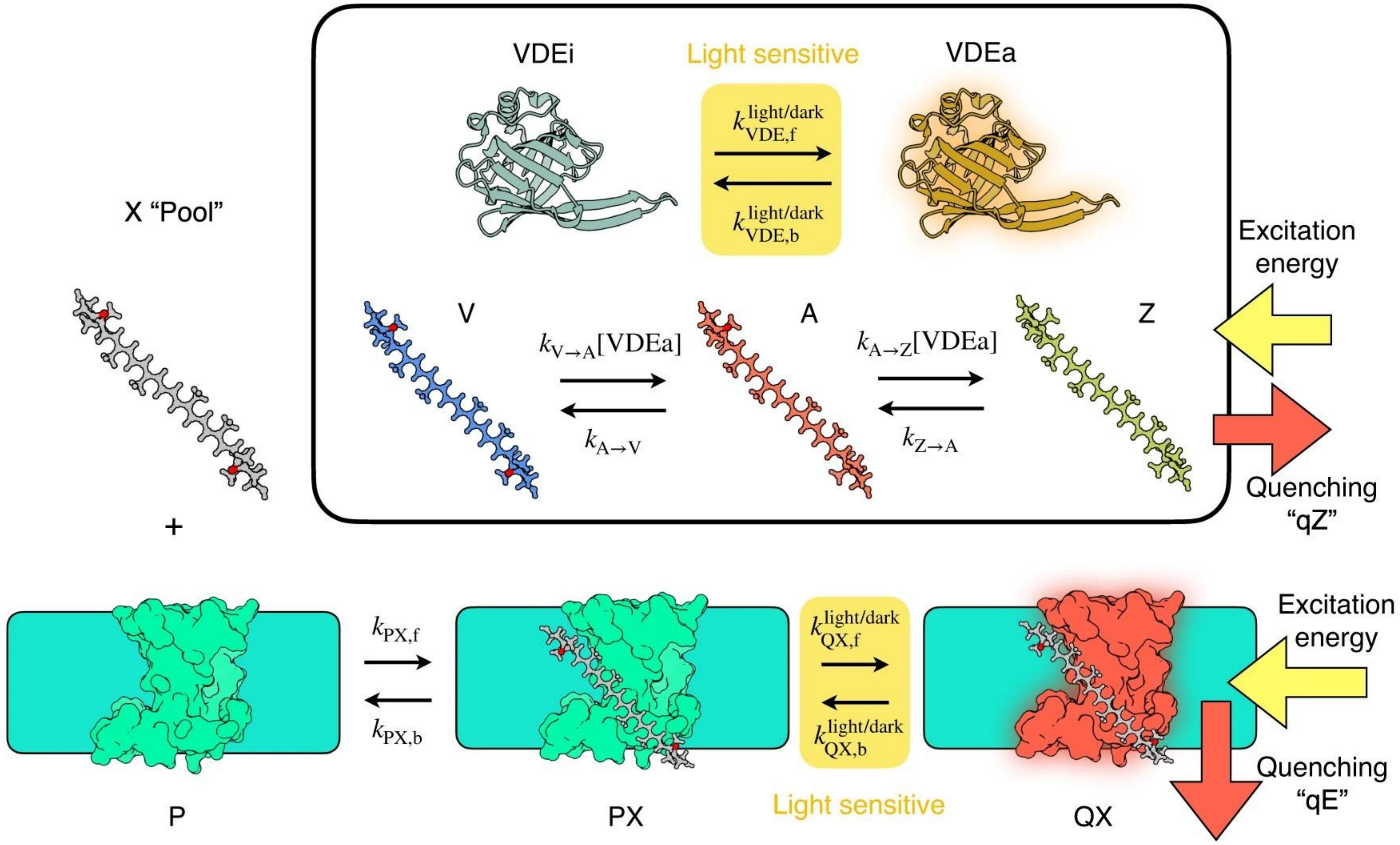
De Souza, A. P. et al. Soybean photosynthesis and crop yield are improved by accelerating recovery from photoprotection. Science (80-.). 377, 851–854 (2022).

Molecular actors in NPQ

Specific **light-harvesting proteins + carotenoids** control NPQ



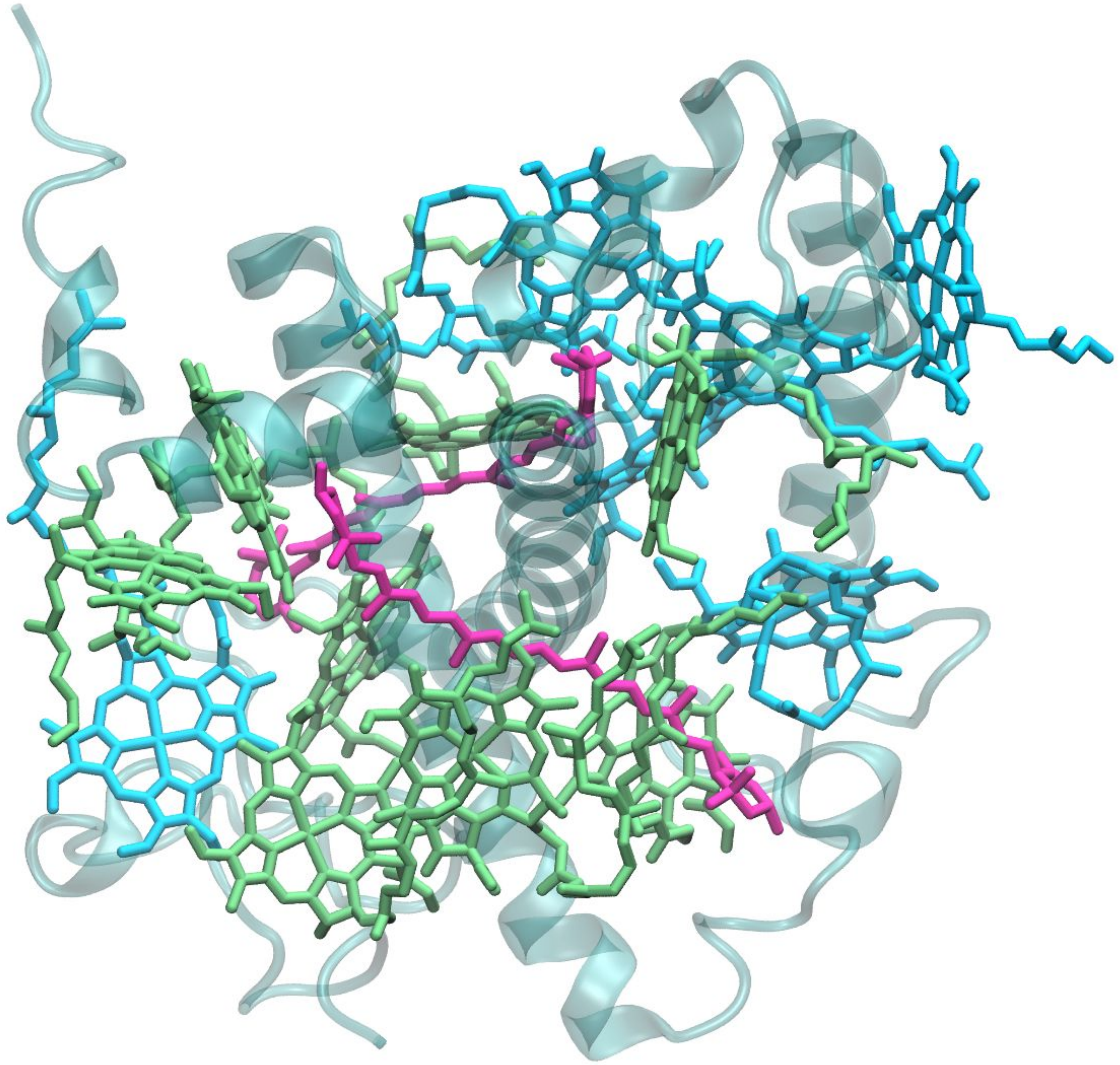
Organism can activate and deactivate **non-photochemical quenching (NPQ)**



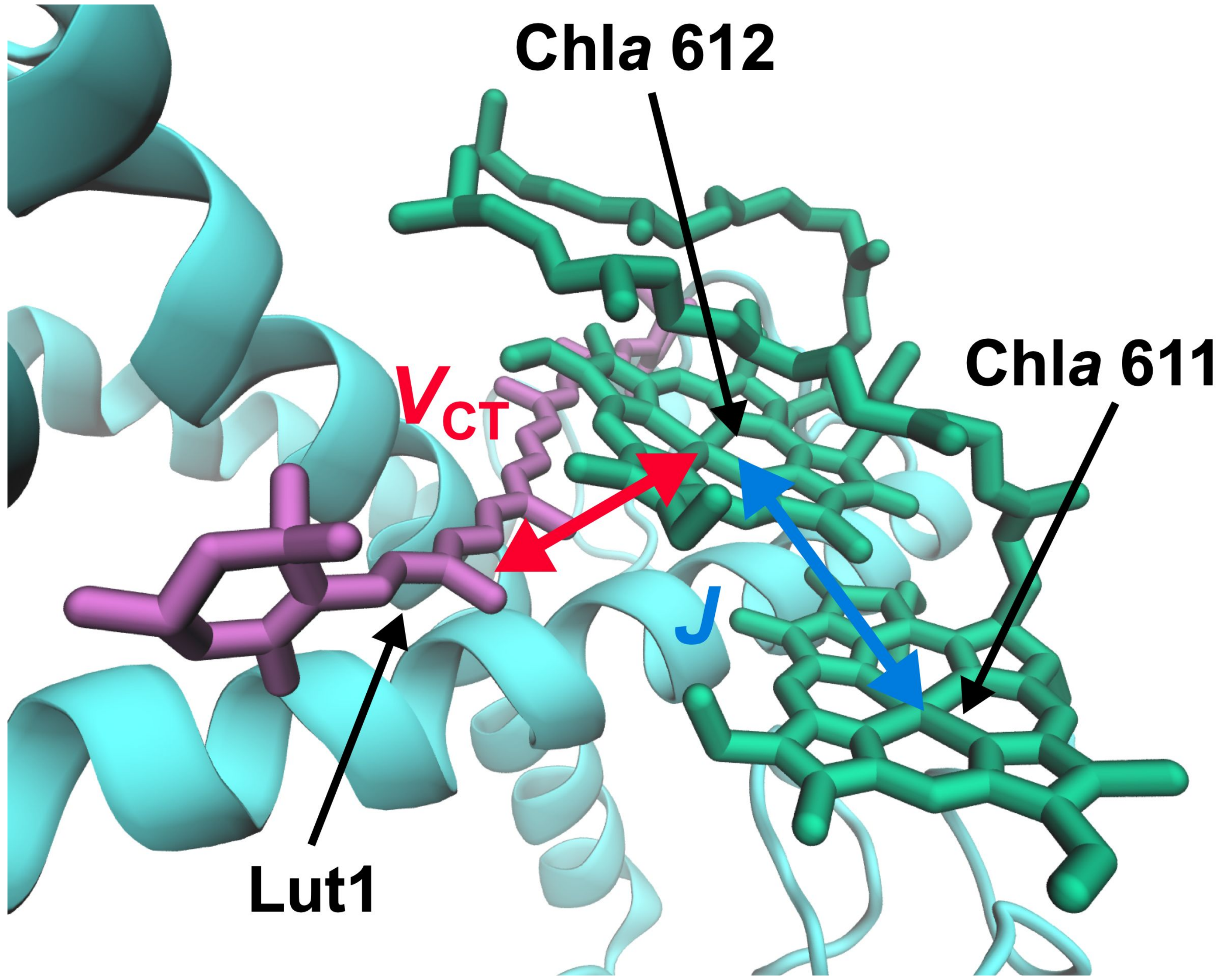
Short, A., Fay, T.P., Crisanto, T. *et al.* Kinetics of the xanthophyll cycle and its role in photoprotective memory and response. *Nat Commun* **14**, 6621 (2023).

Exciton quenching in photosynthesis

LHCII plays a role in NPQ in plants



Lutein in LHCII



Cupellini, L., Calvani, D., Jacquemin, D. & Mennucci, B. *Nat. Commun.* **11**, 662 (2020).

Charge transfer quenching with carotenoids

Carotenoids (e.g. lutein) act as quenchers via **charge transfer**

How can we model the **coupled excitation energy transfer dynamics** and **charge transfer quenching**?

Energy dissipated as heat

Park, S. *et al. Proc. Natl. Acad. Sci.* **116**, 3385–3390 (2019).

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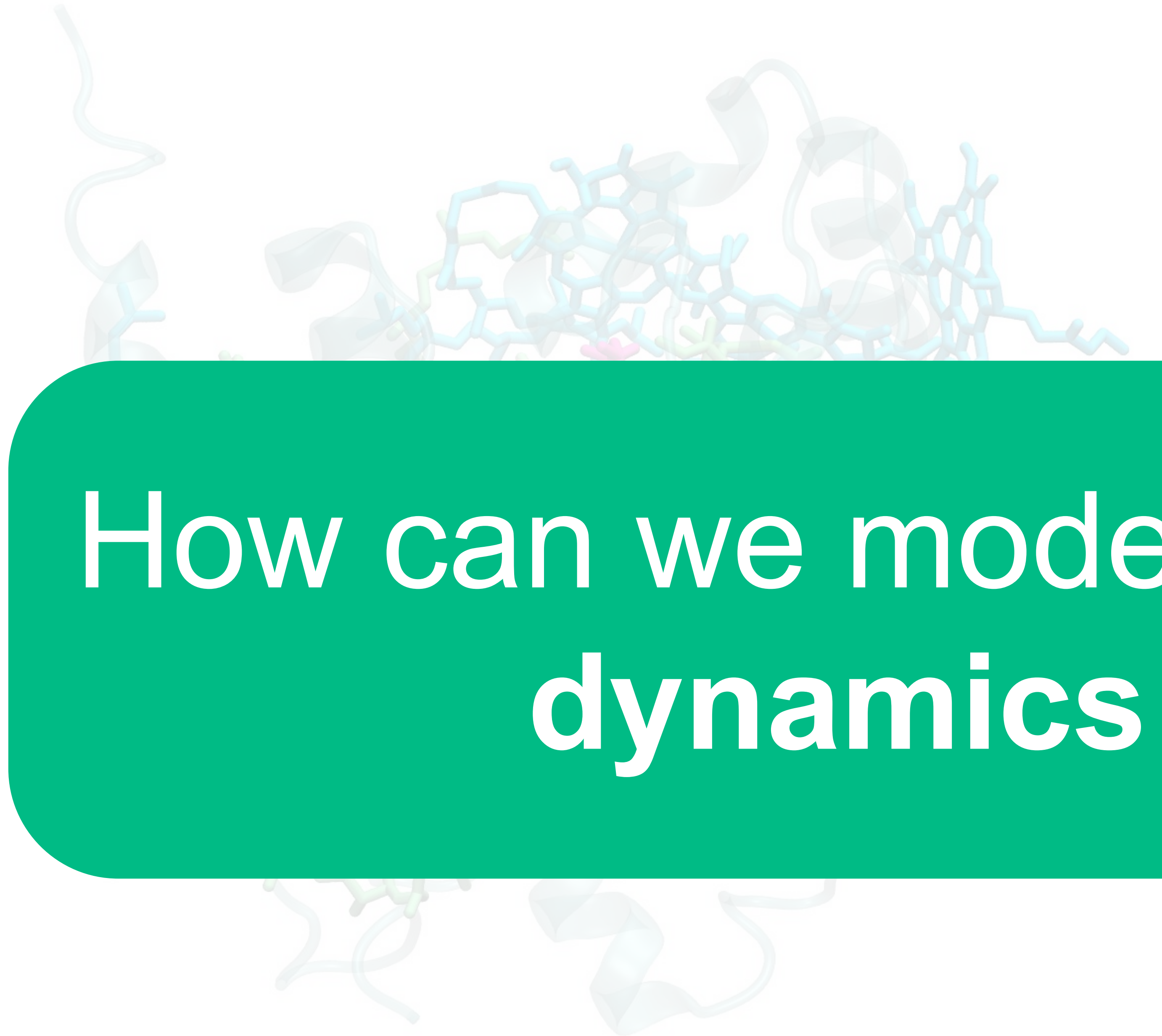
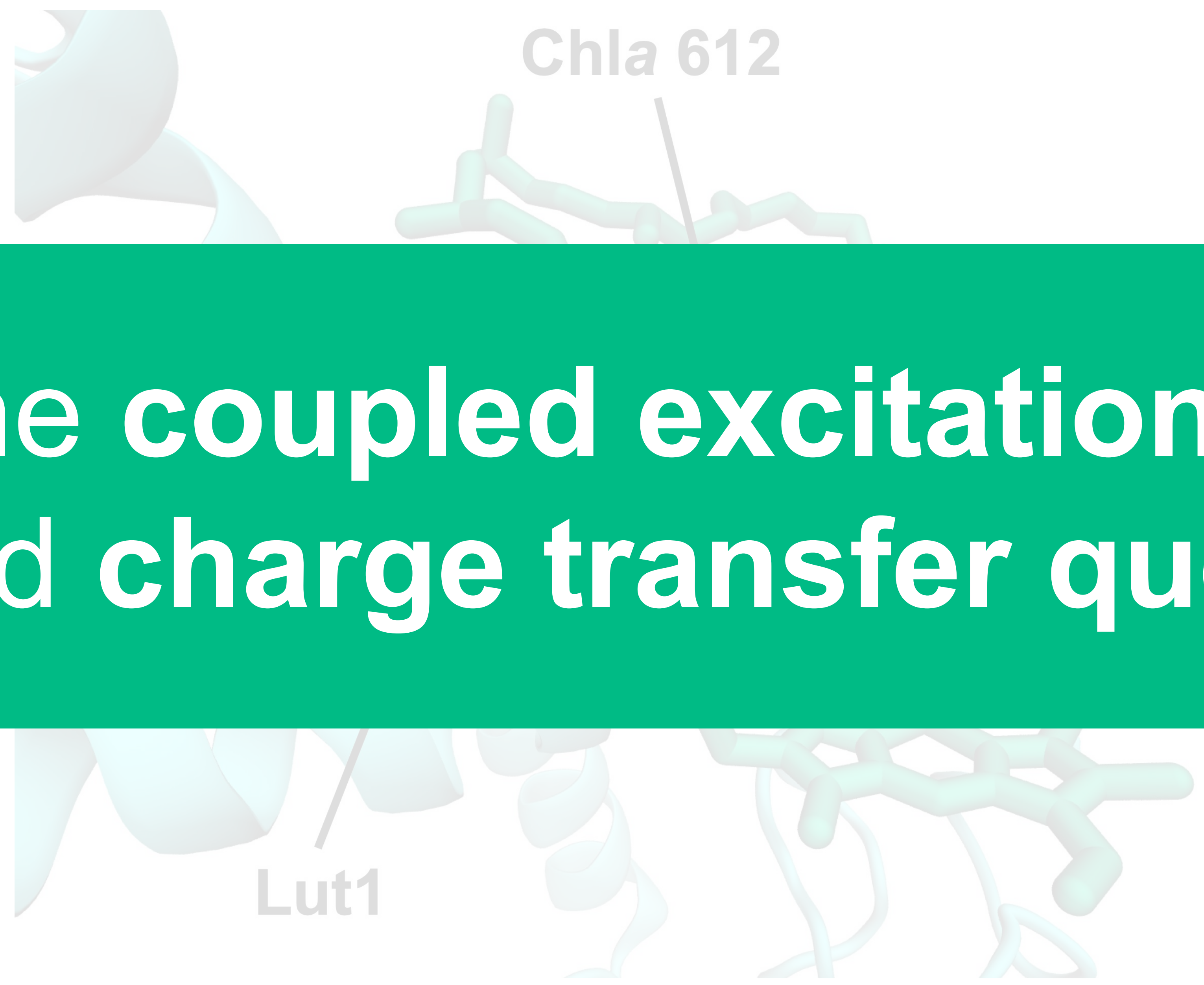
Energy transfer





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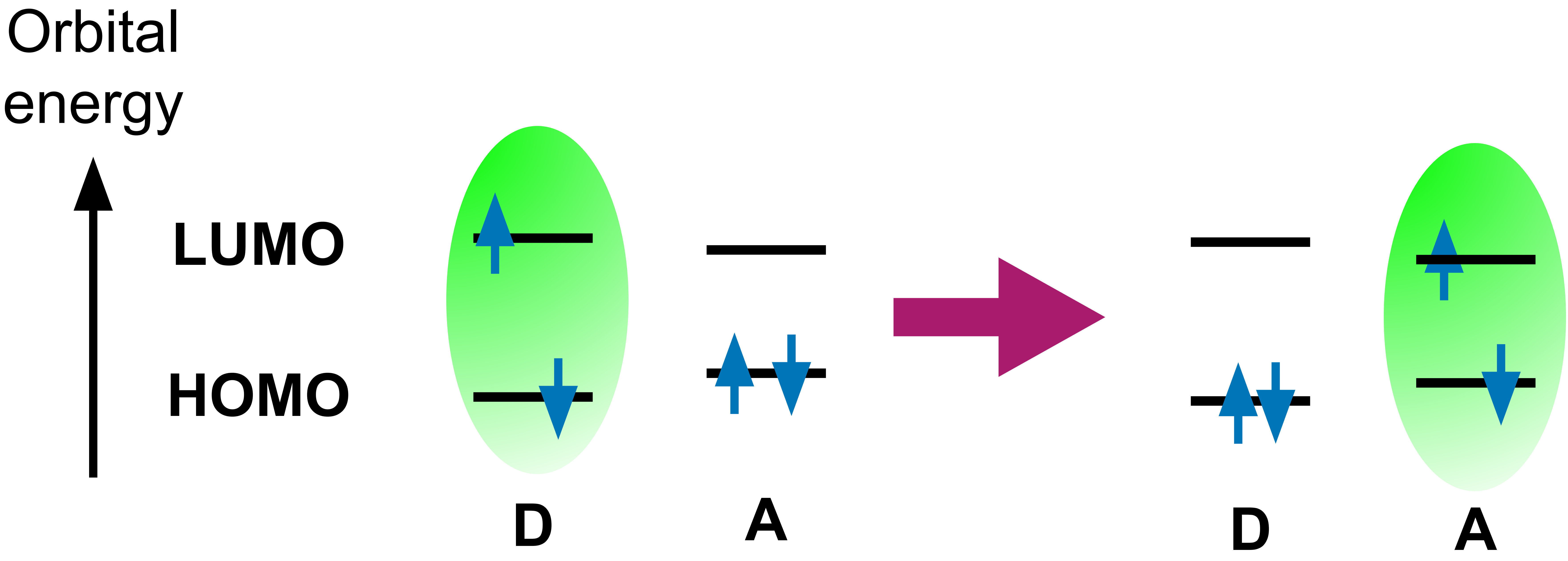
Energy transfer *vs* electron transfer

Excitation energy transfer (EET)

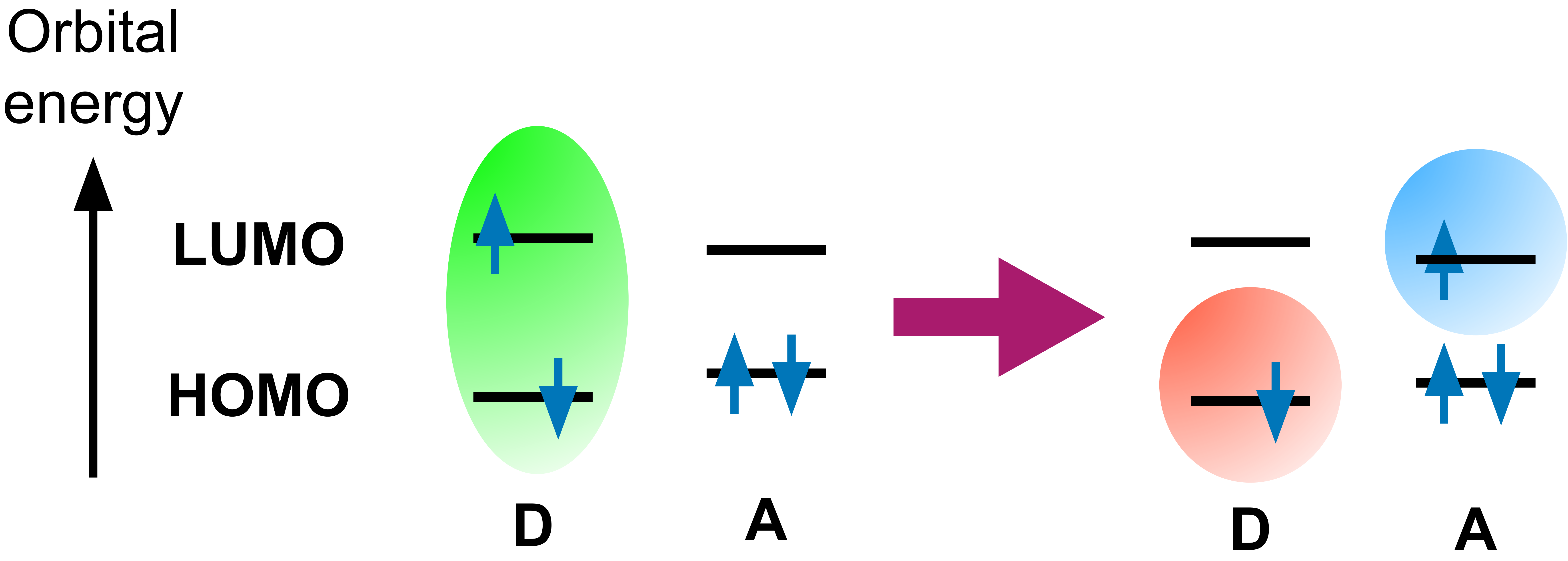


Coupling between excited states mediated by **electrostatics**

Weak coupling to molecular **environment**

Energy transfer *vs* electron transfer

Electron/charge transfer (CT)



Coupling between states mediated by **orbital overlap**

Strong coupling to molecular **environment**

Hybrid (strong-coupling) method

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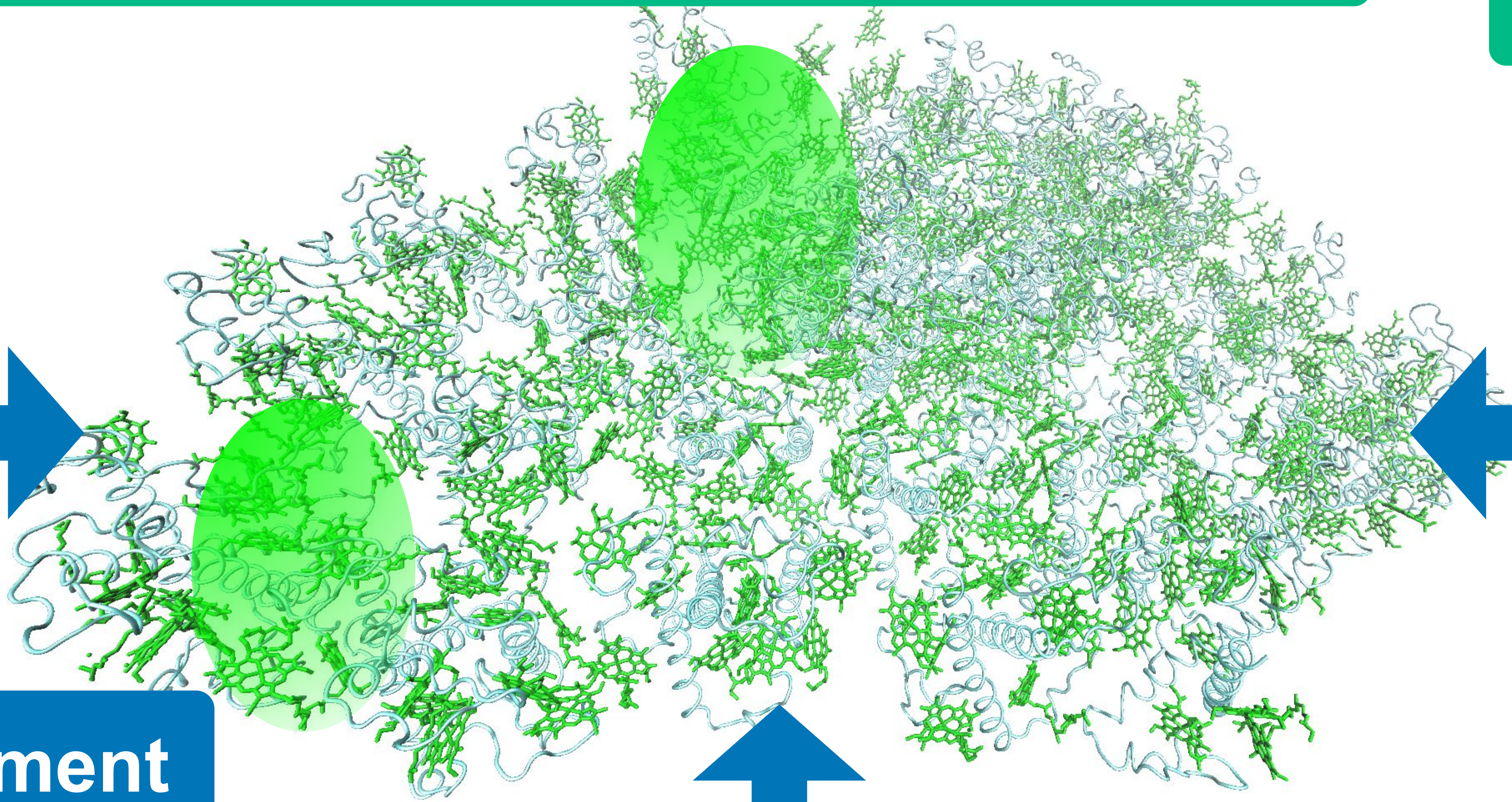
Open system of interest: system+bath

HEOM, QUAPI, ACE, TEMPO…



Charge transfer

Radiation field

Perturbative treatment of loss processes fully accounting for **non-Markovian open system dynamics**

Non-radiative decay

Exciton quenching in photosynthesis

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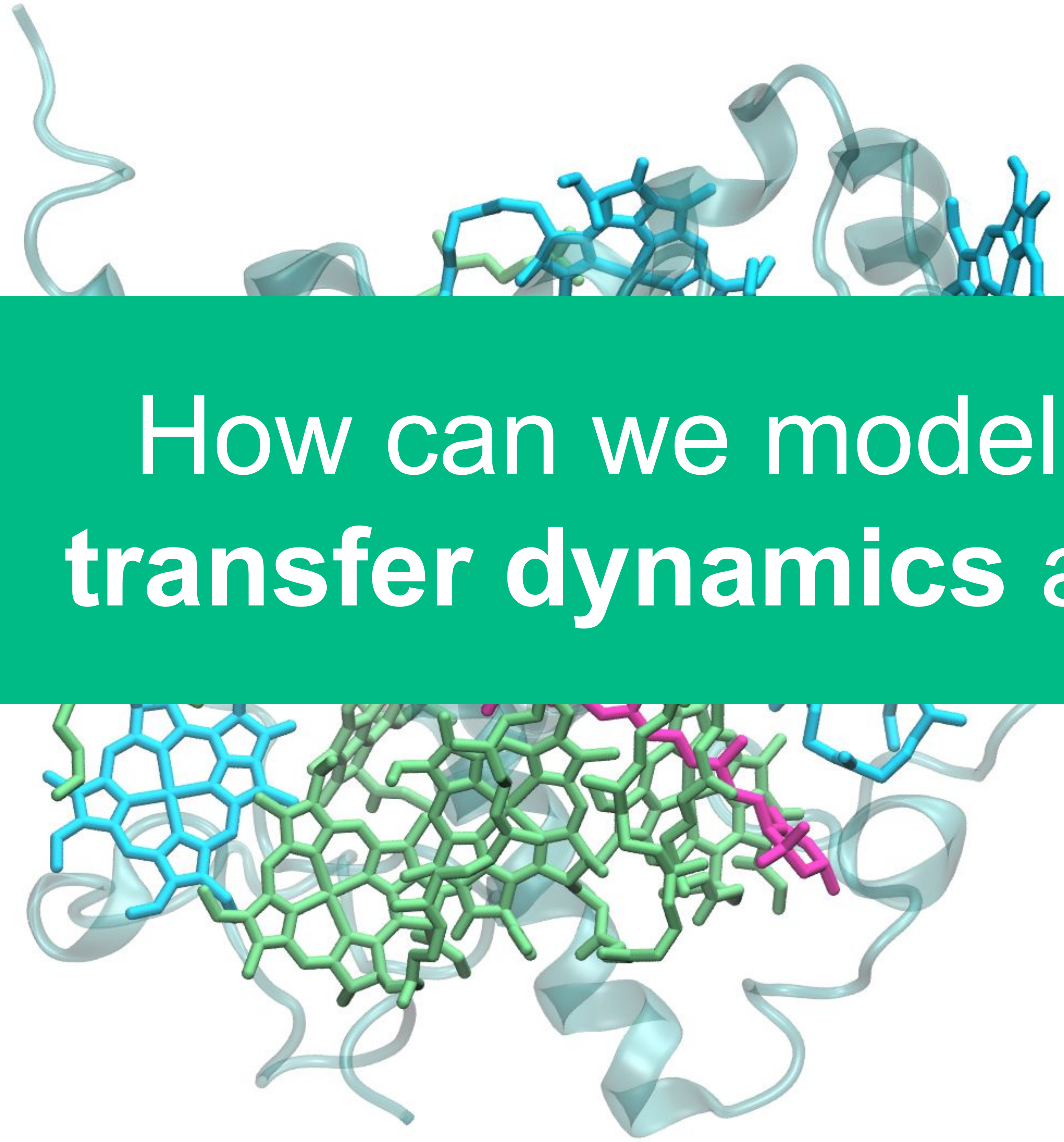
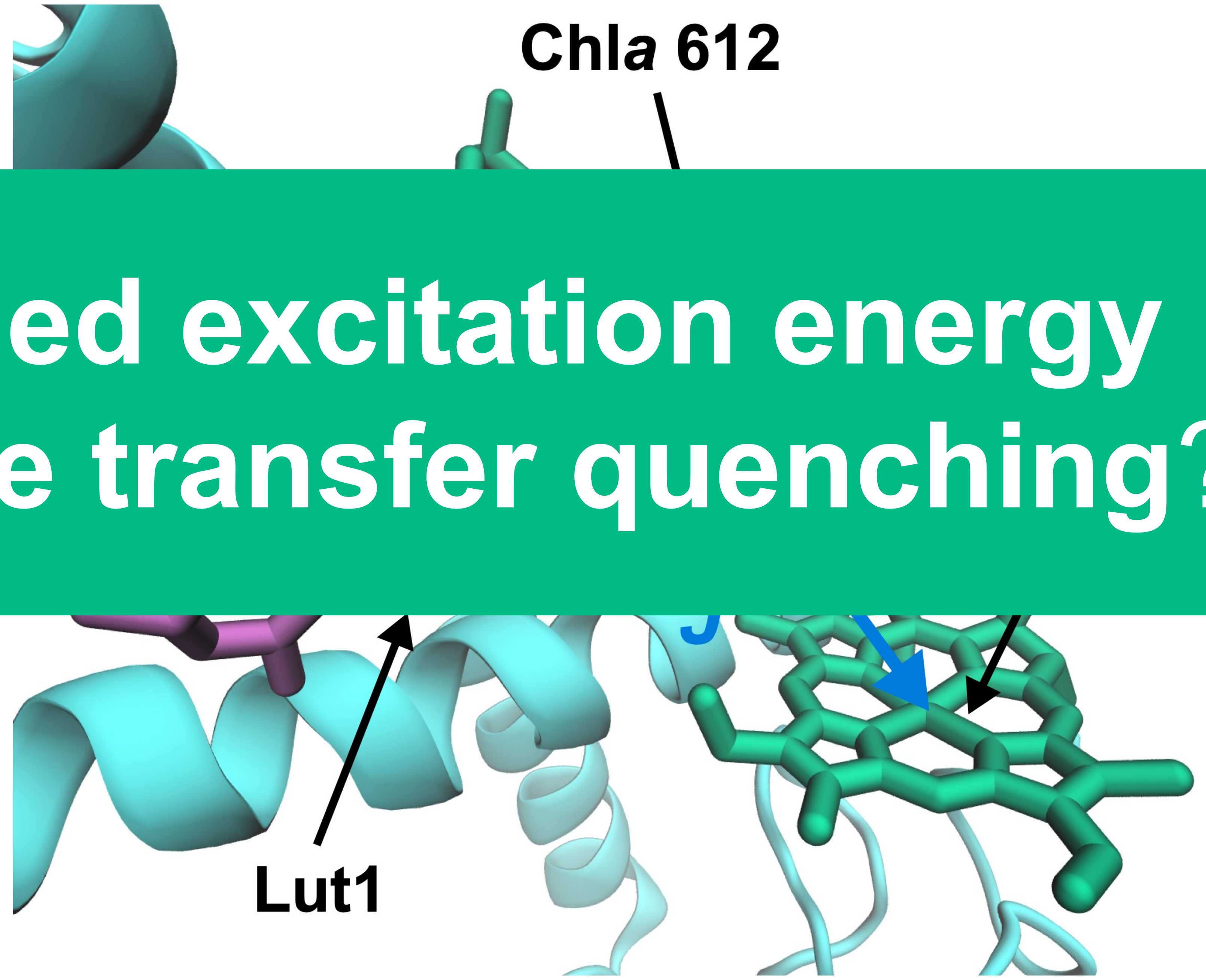


Lutein in LHCII



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Exciton quenching

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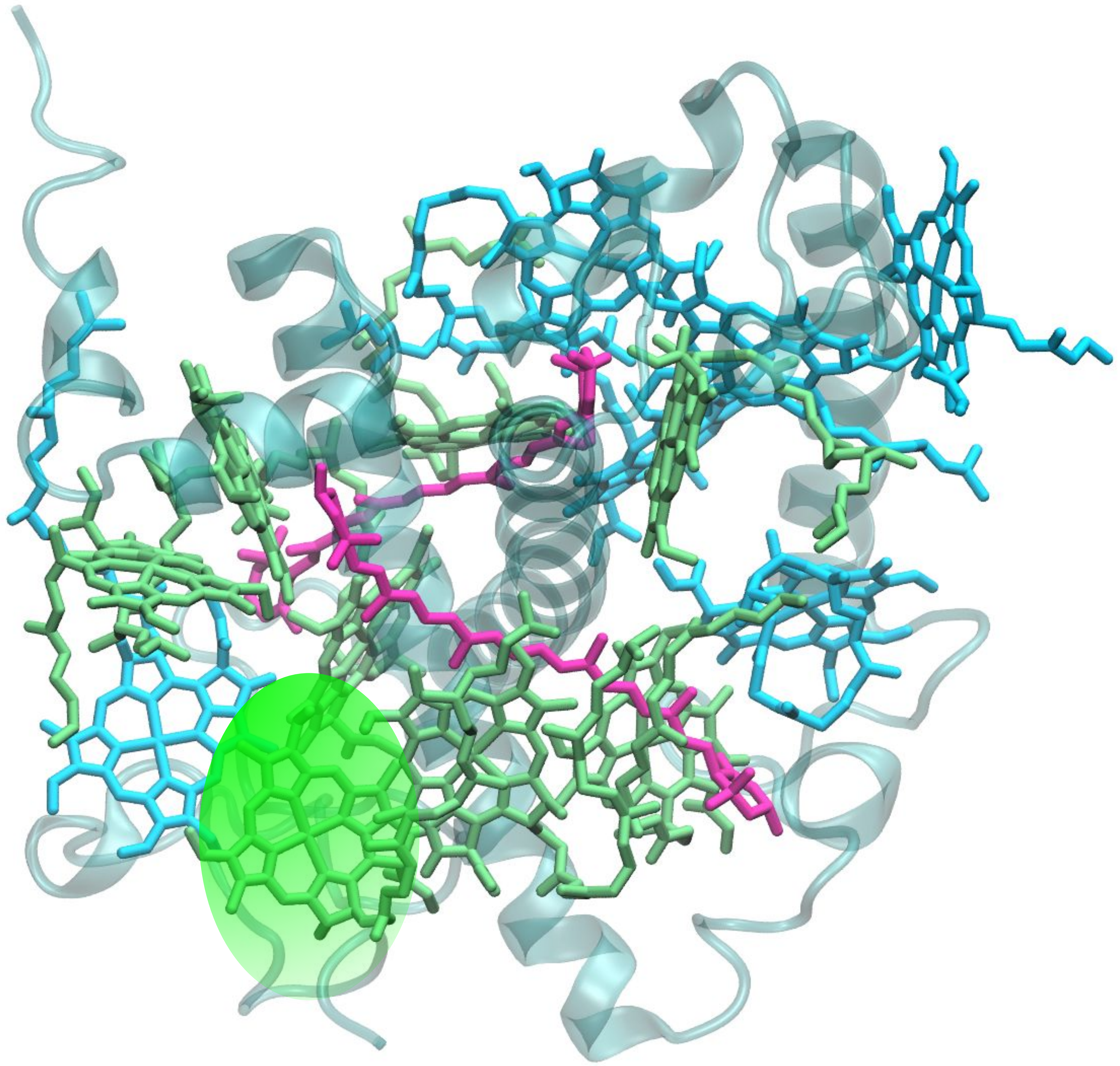
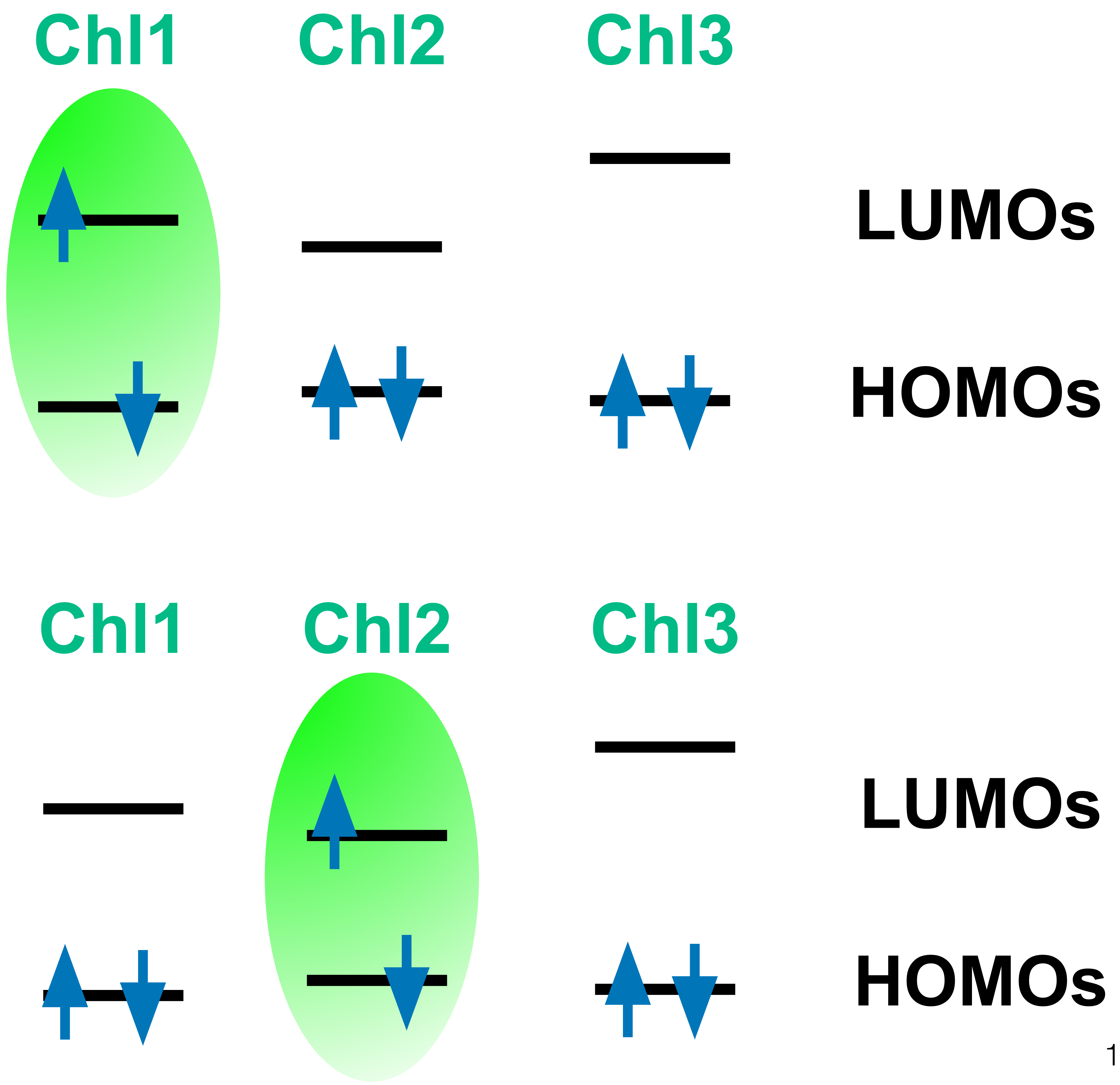
How do we describe **excitation energy transfer dynamics**?

Exciton quenching in photosynthesis

Locally excited (**LE**) states





Exciton quenching in photosynthesis

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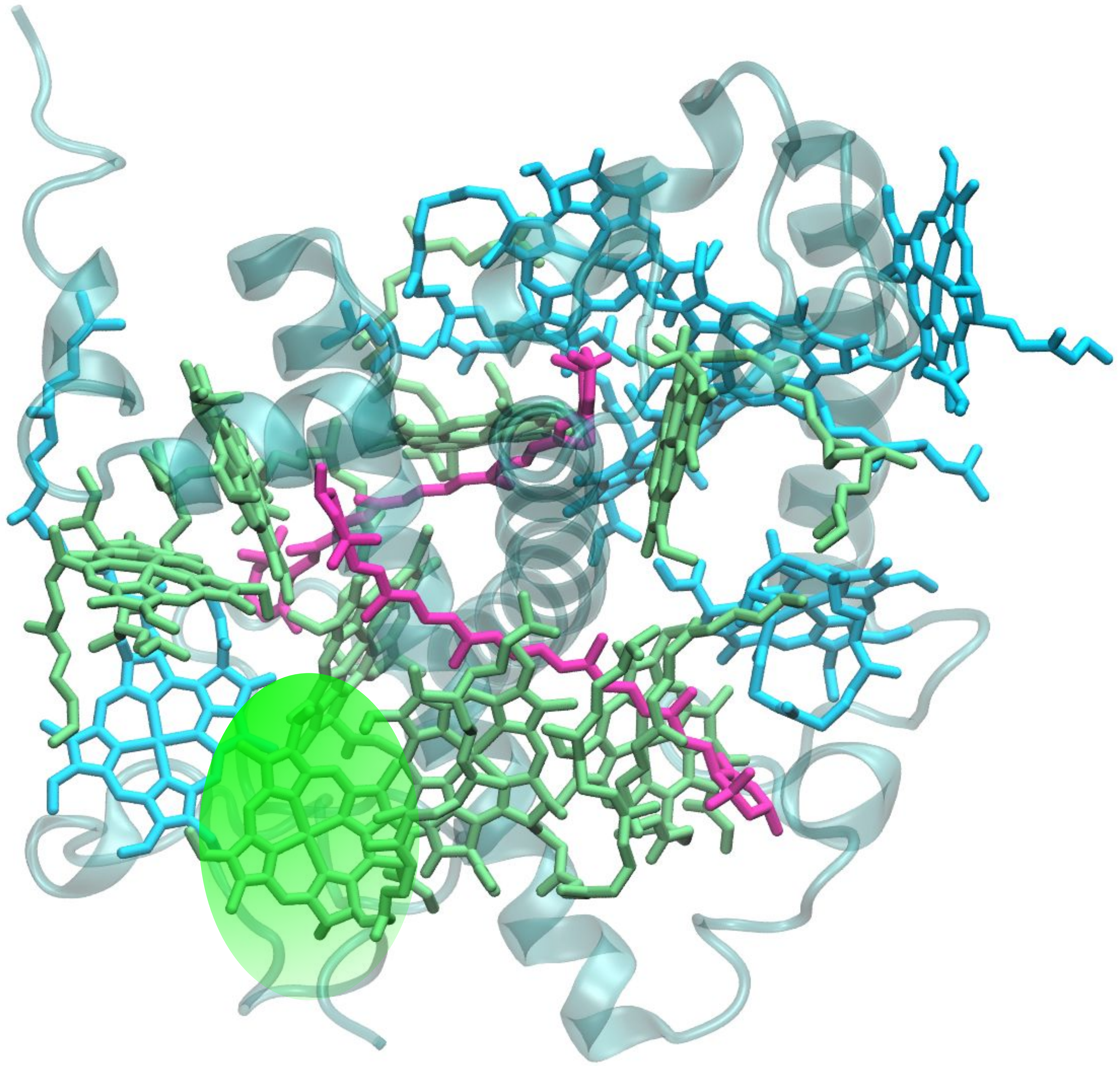
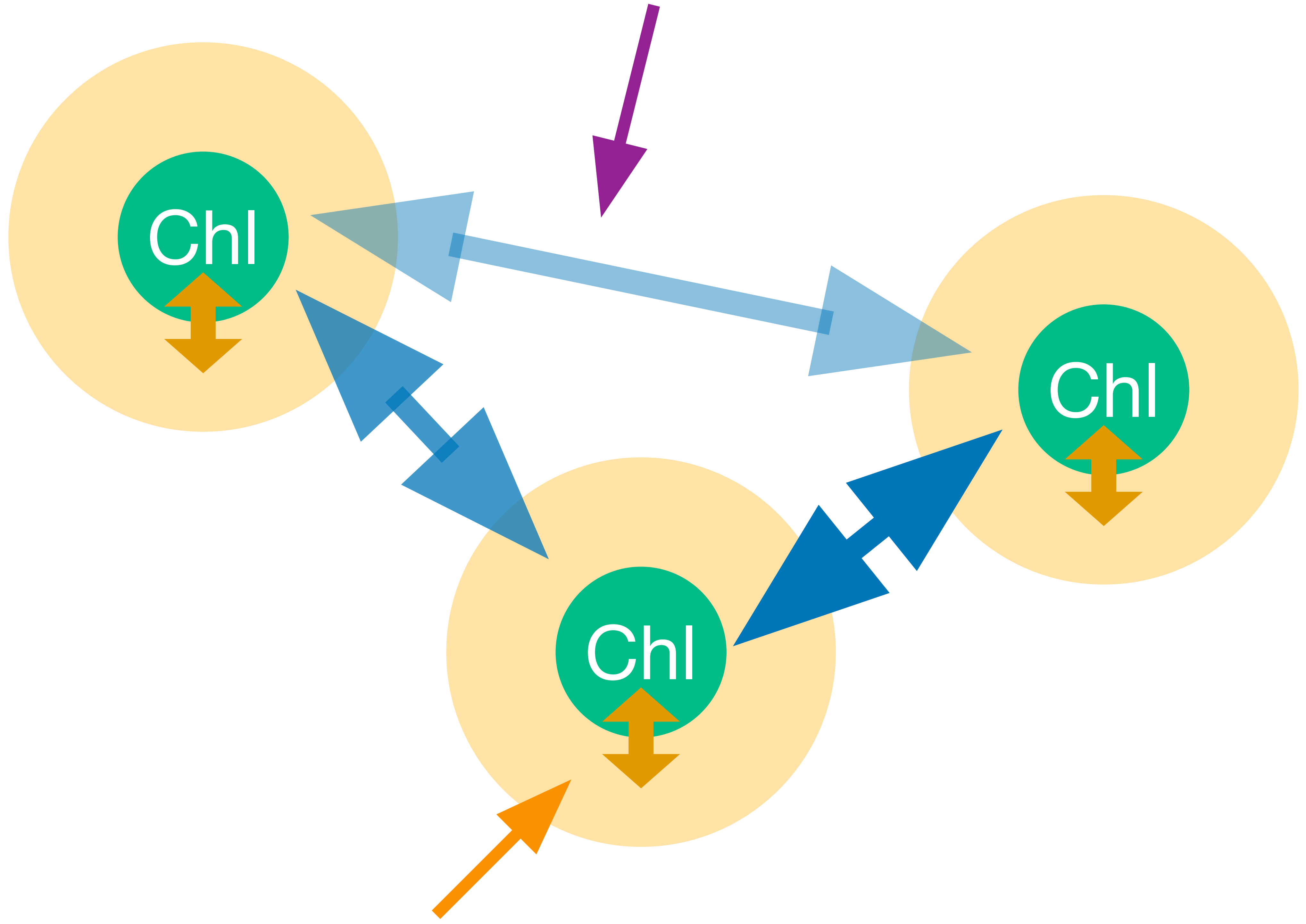


Local excitations **couple to each other** (dipole-dipole interaction) forming **delocalised excitons**



Coupling to vibrations on the chromophore
Reorganisation energy:

Exciton quenching in photosynthesis

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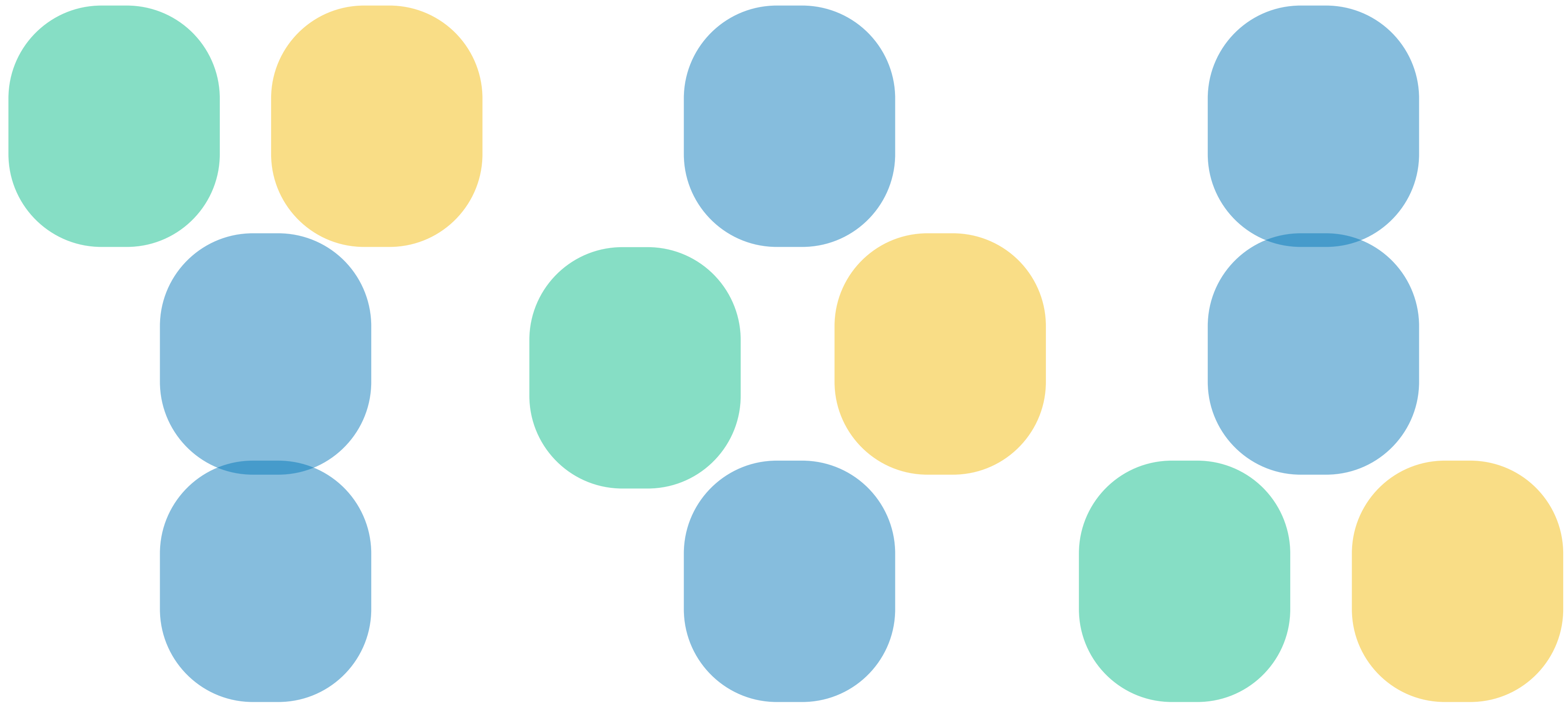
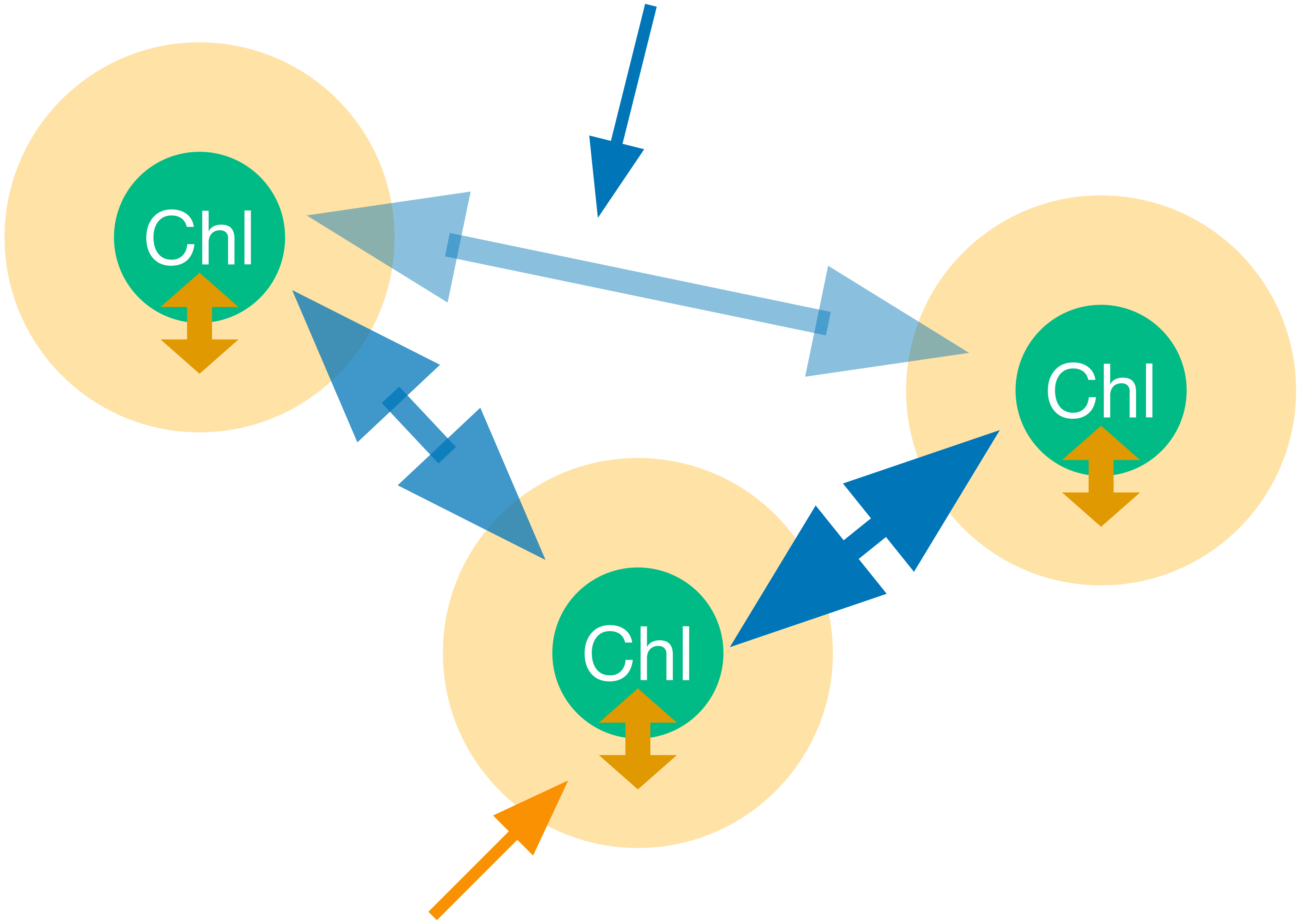
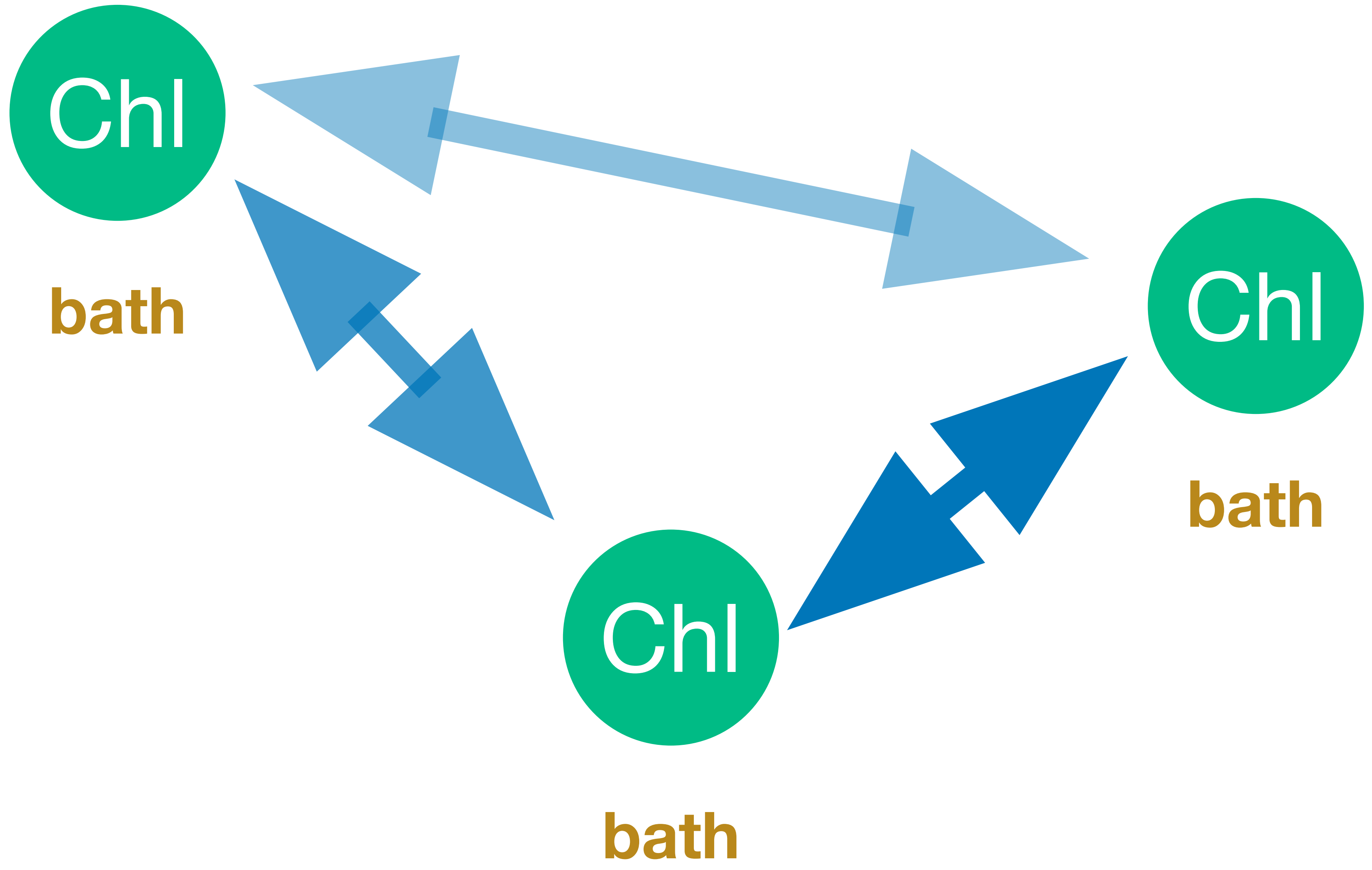
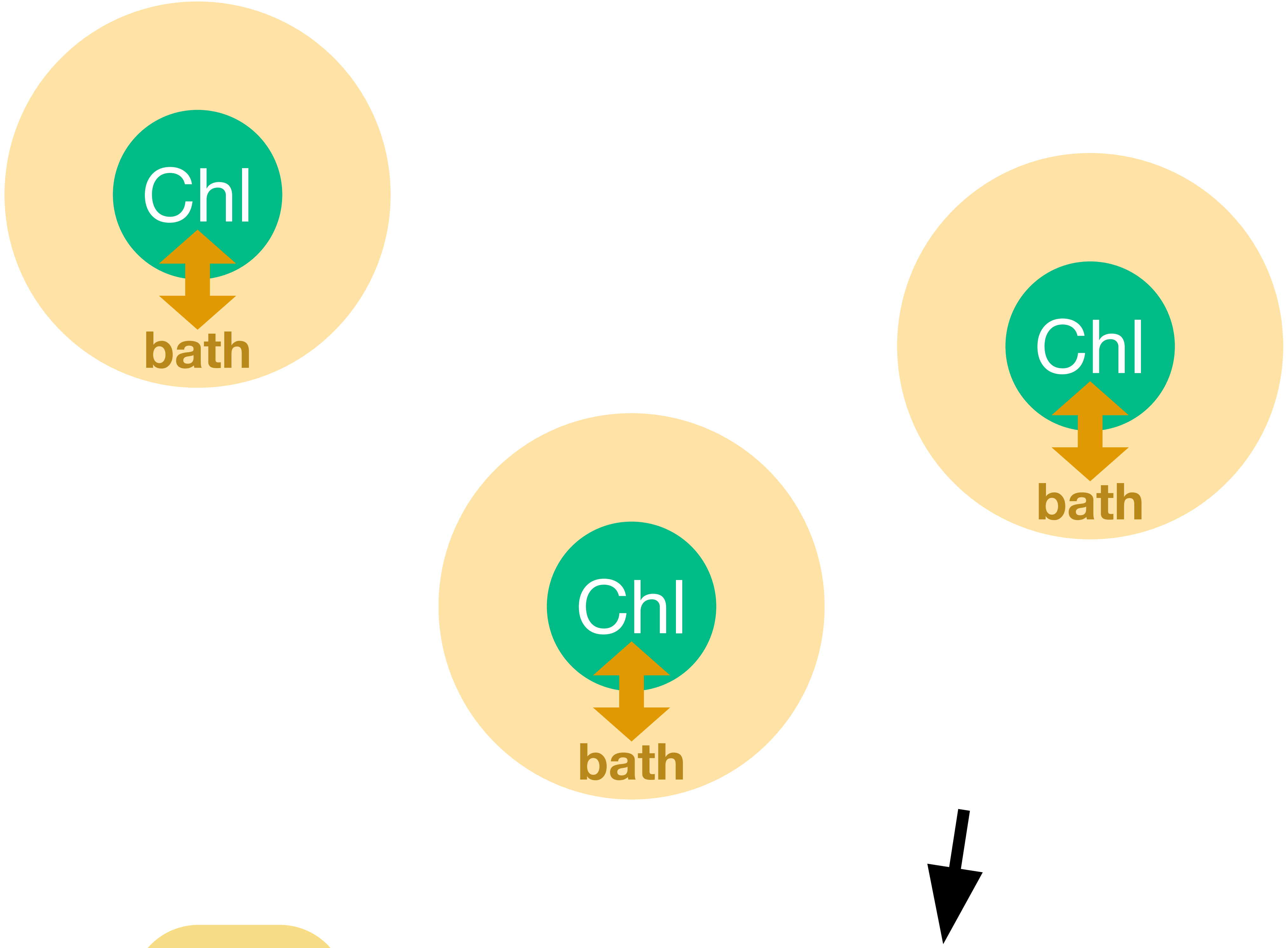




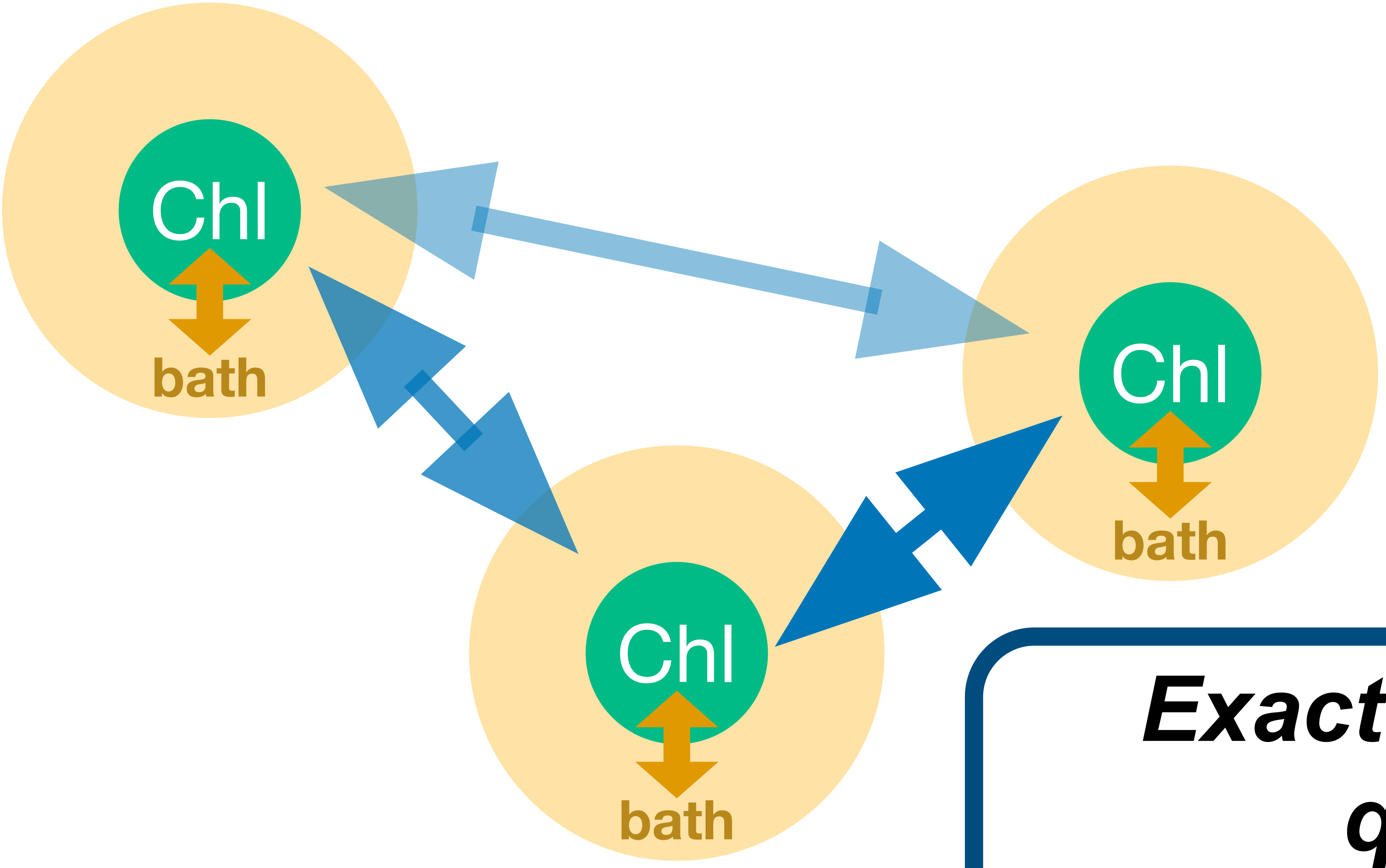
Coupling to vibrations on the chromophore
Reorganisation energy:

Excitons in protein-pigment complexes





Excitation energy transport



Approximate theories

Förster theory
(hopping)

Redfield theory
(coherent transport)

Exact non-markovian/non-perturbative quantum dynamics approach

Hierarchical equation of motion (HEOM)

Exciton transport with HEOM

Hierarchical equations of motion (HEOM)

Large reorganisation energies → Deeper hierarchies → Higher computational cost

density operat

Tanimura, Y. & Kubo, R. *J. Phys. Soc. Japan* **58**, 101–114 (1989).

Exciton quenching

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How do model **charge transfer quenching** efficiently?

Charge transfer quenching model

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Coupled charge and energy transfer dynamics in light harvesting complexes from a hybrid hierarchical equations of motion approach

Cite as: J. Chem. Phys. **157**, 174104 (2022); https://doi.org/10.1063/5.0117659
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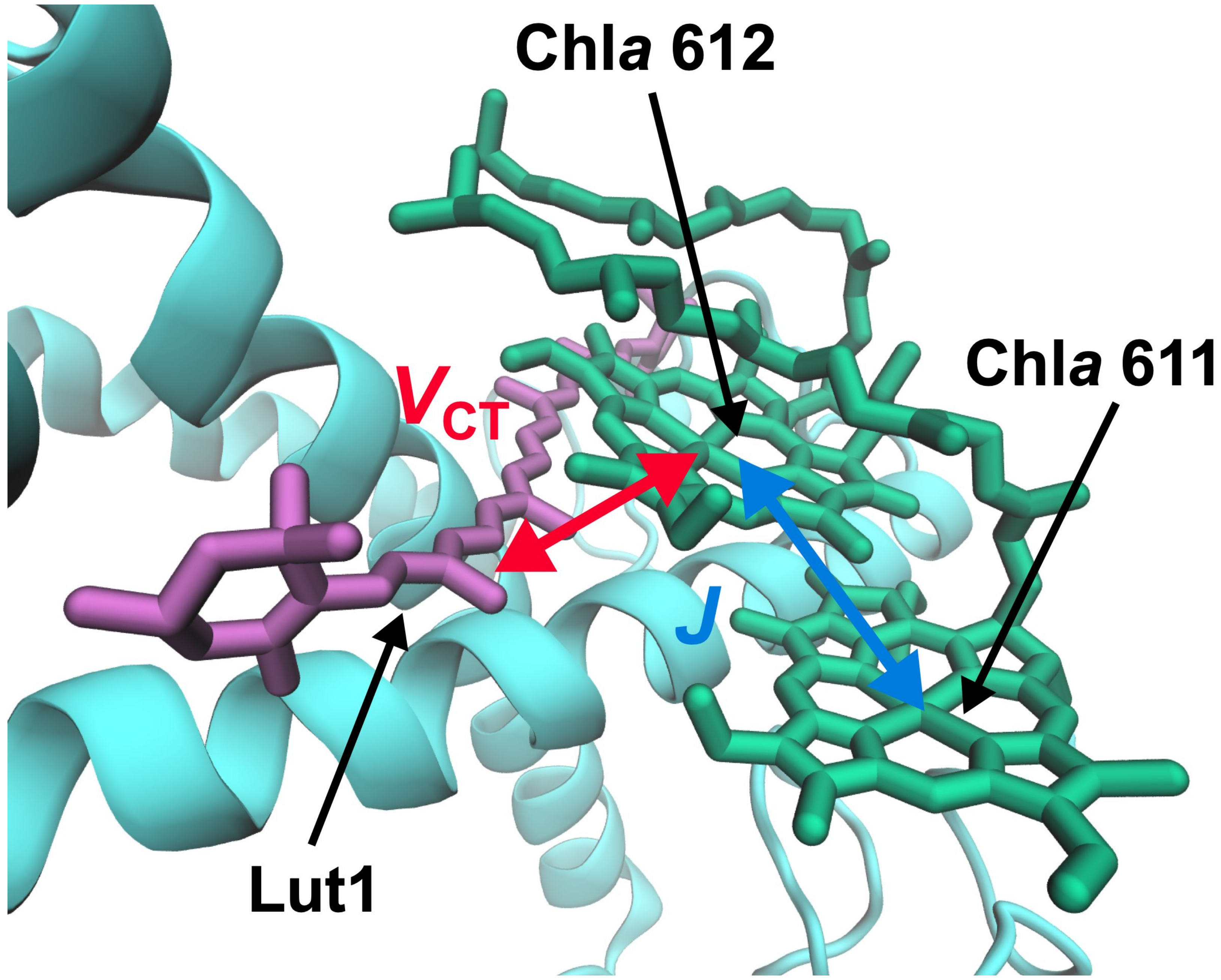
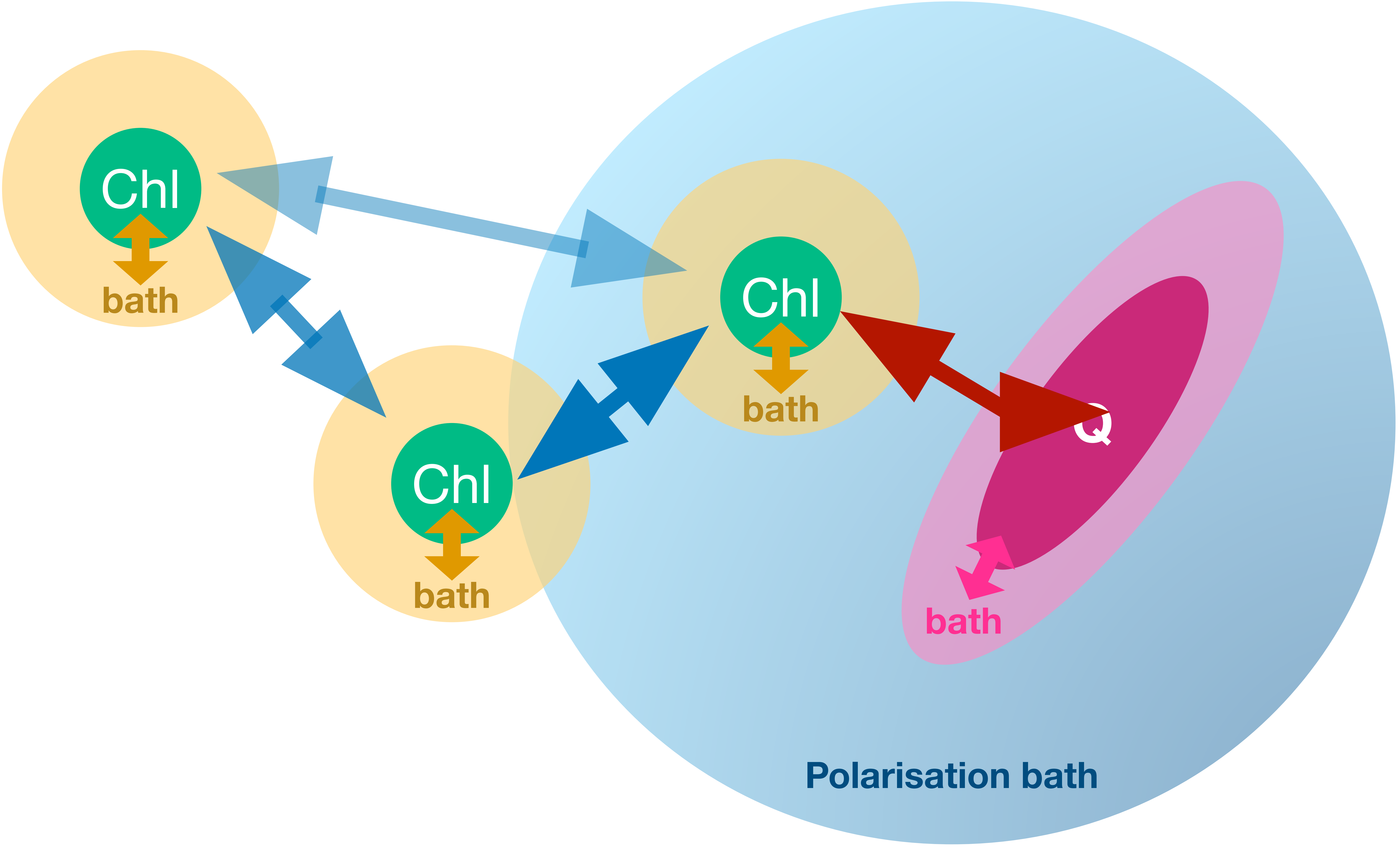
Thomas P. Fay and David T. Limmer

TPF and D.T. Limmer, *J. Chem. Phys.* **157**, 174104 (2022).



Charge transfer quenching model



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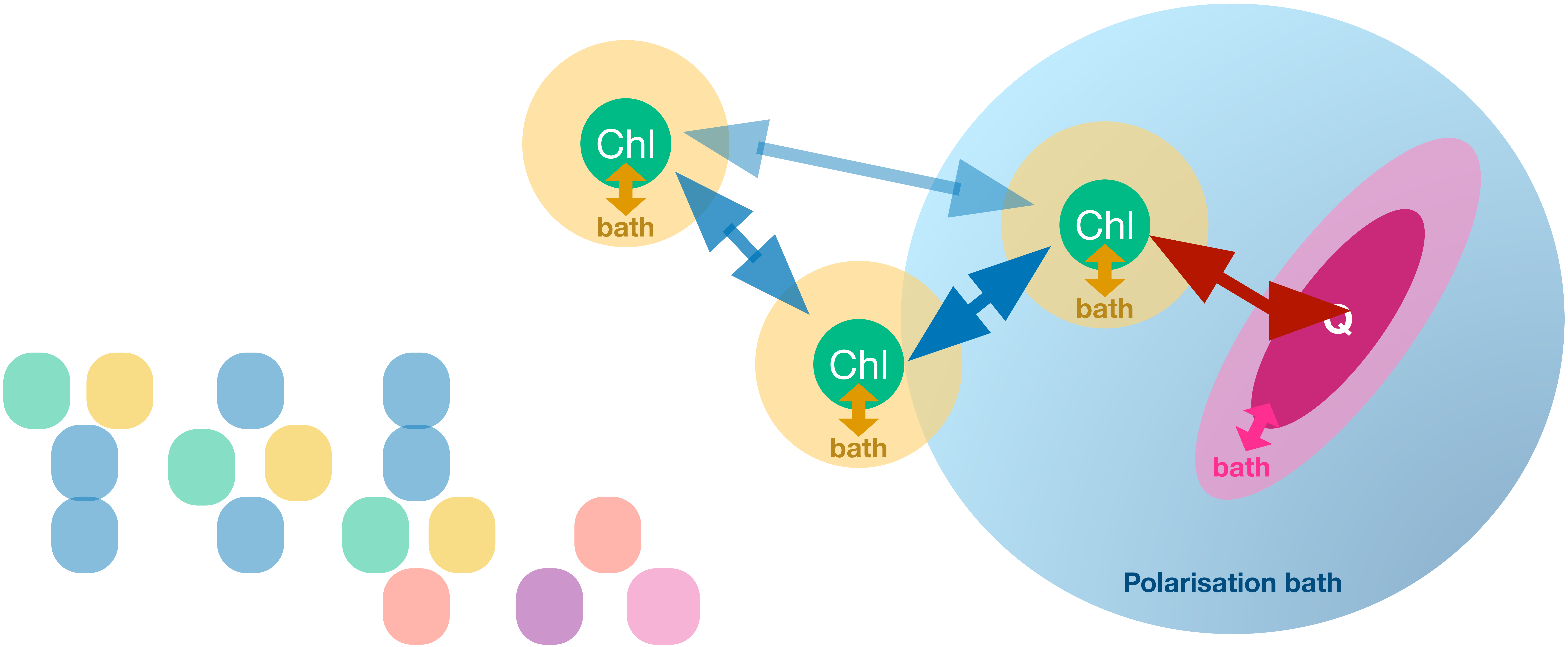
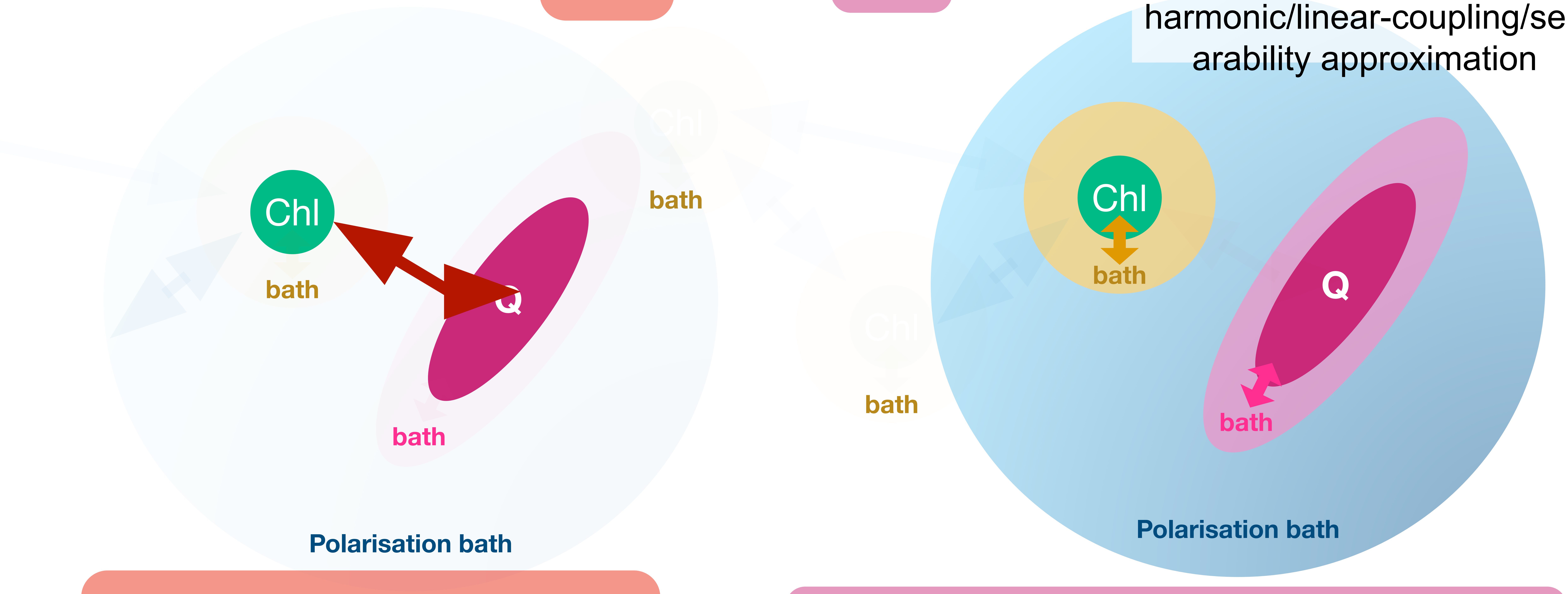
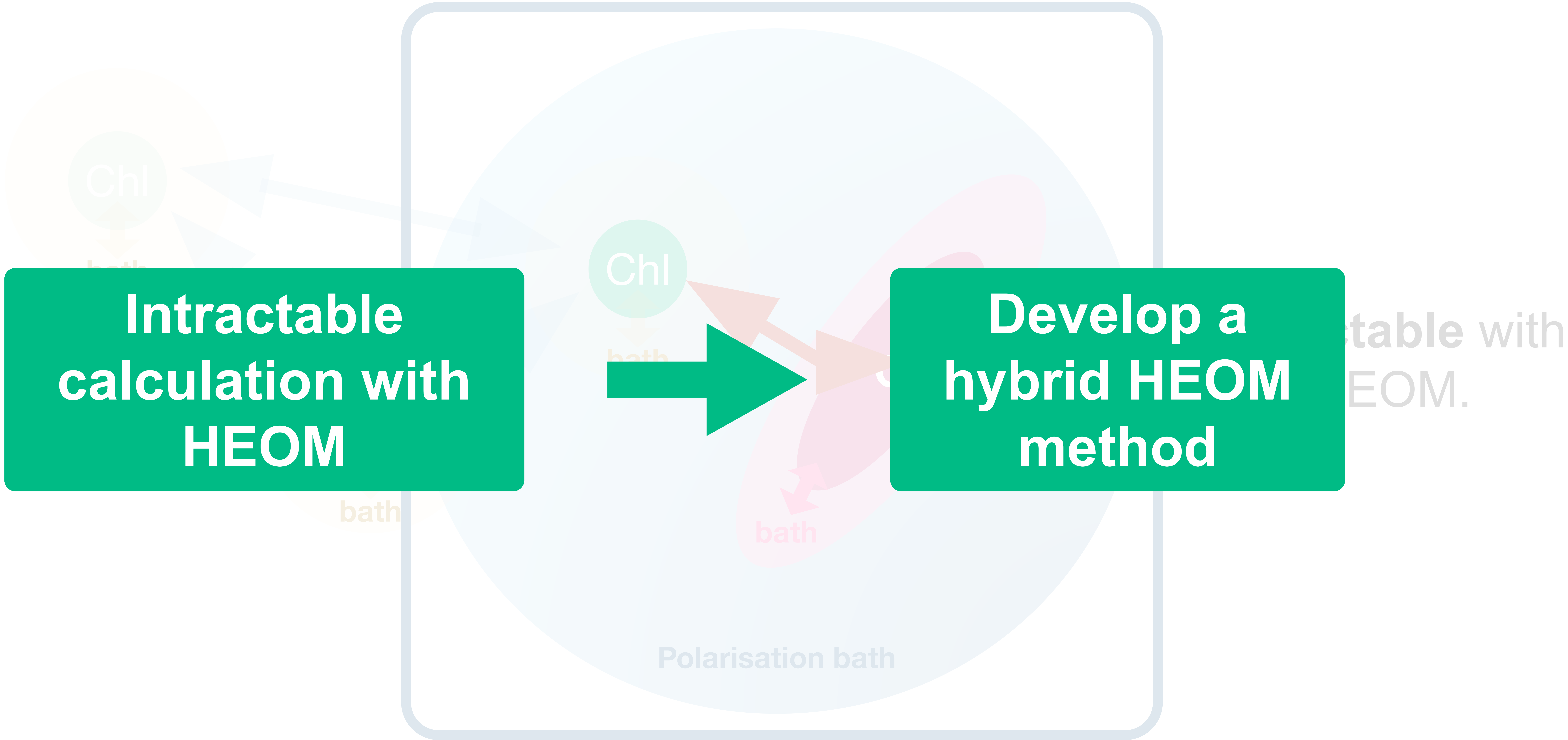


Charge transfer quenching model

No harmonic/linear-coupling/separability approximation



CT is intractable with HEOM



Hybrid HEOM method

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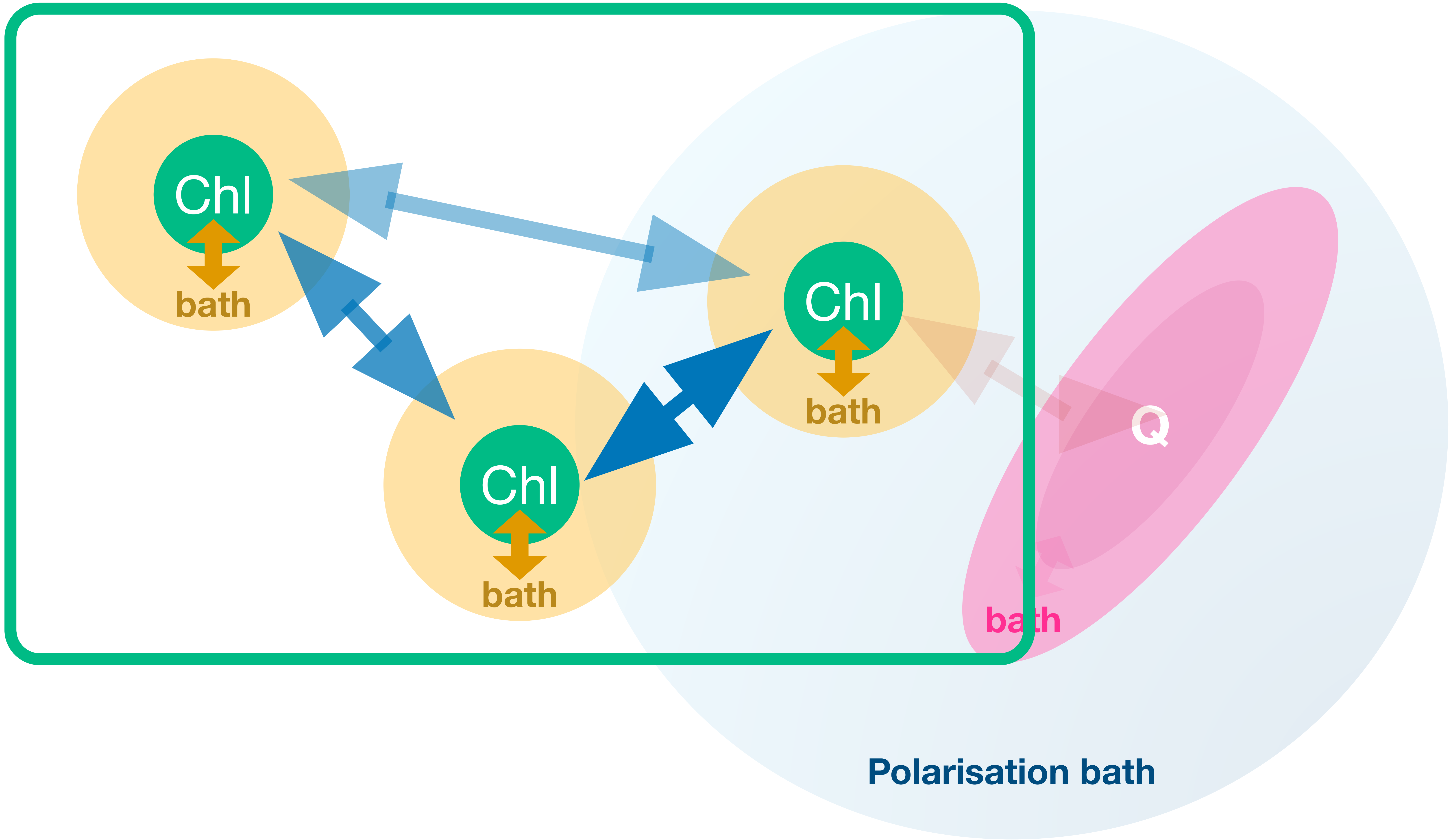
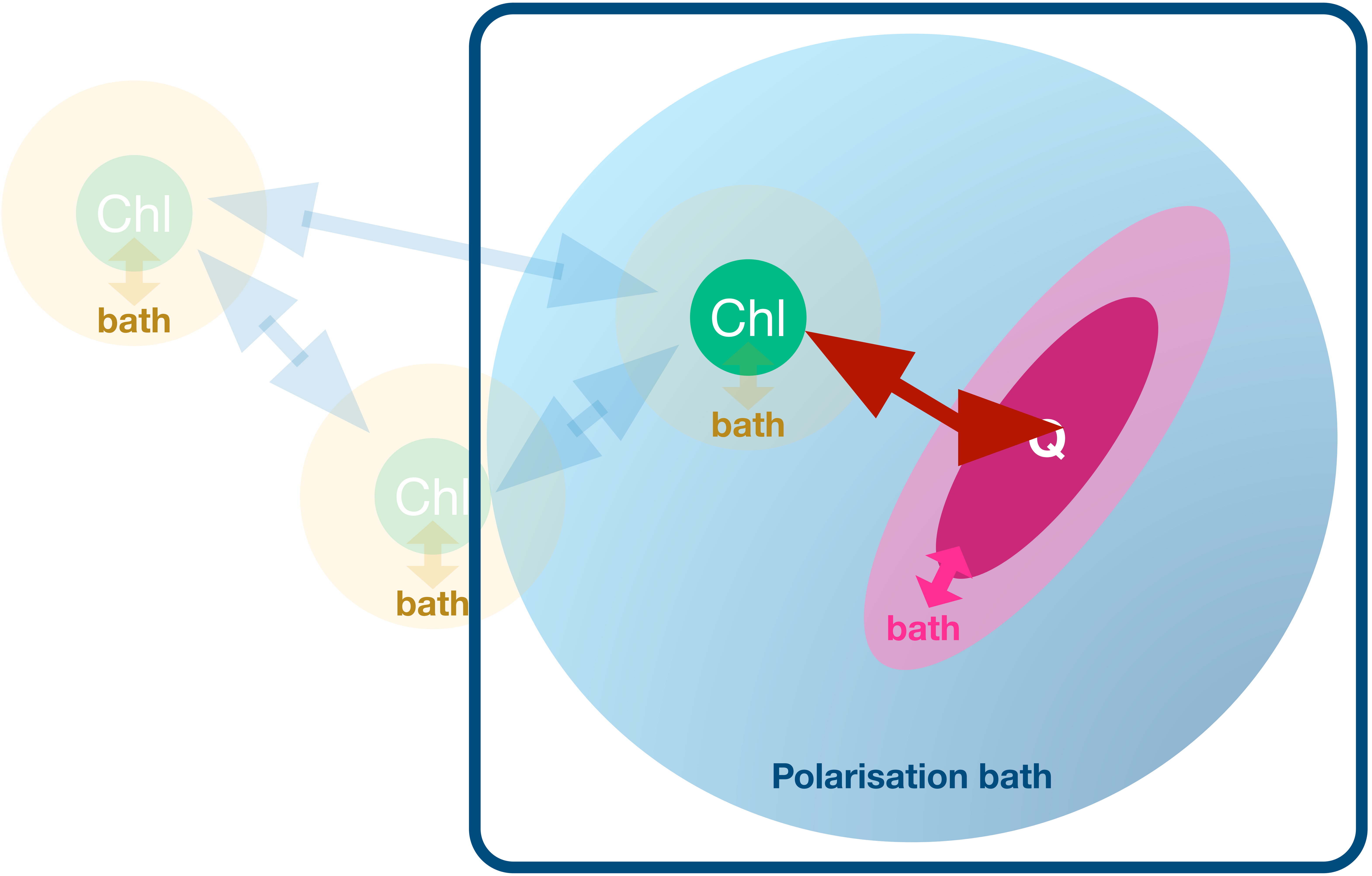


Treat this partition with **HEOM**

Hybrid HEOM method



Treat this partition with **perturbation theory**

Strong coupling QME

Weak *system-bath* coupling

Strong *system-bath* coupling

M. Sparpaglione and S. Mukamel, J. Chem. Phys. 88, 3263 (1988).
TPF, L.P. Lindoy, and D.E. Manolopoulos, J. Chem. Phys. 149, 064107 (2018).
A. Trushechkin, Phys. Rev. A 106, 042209 (2022).

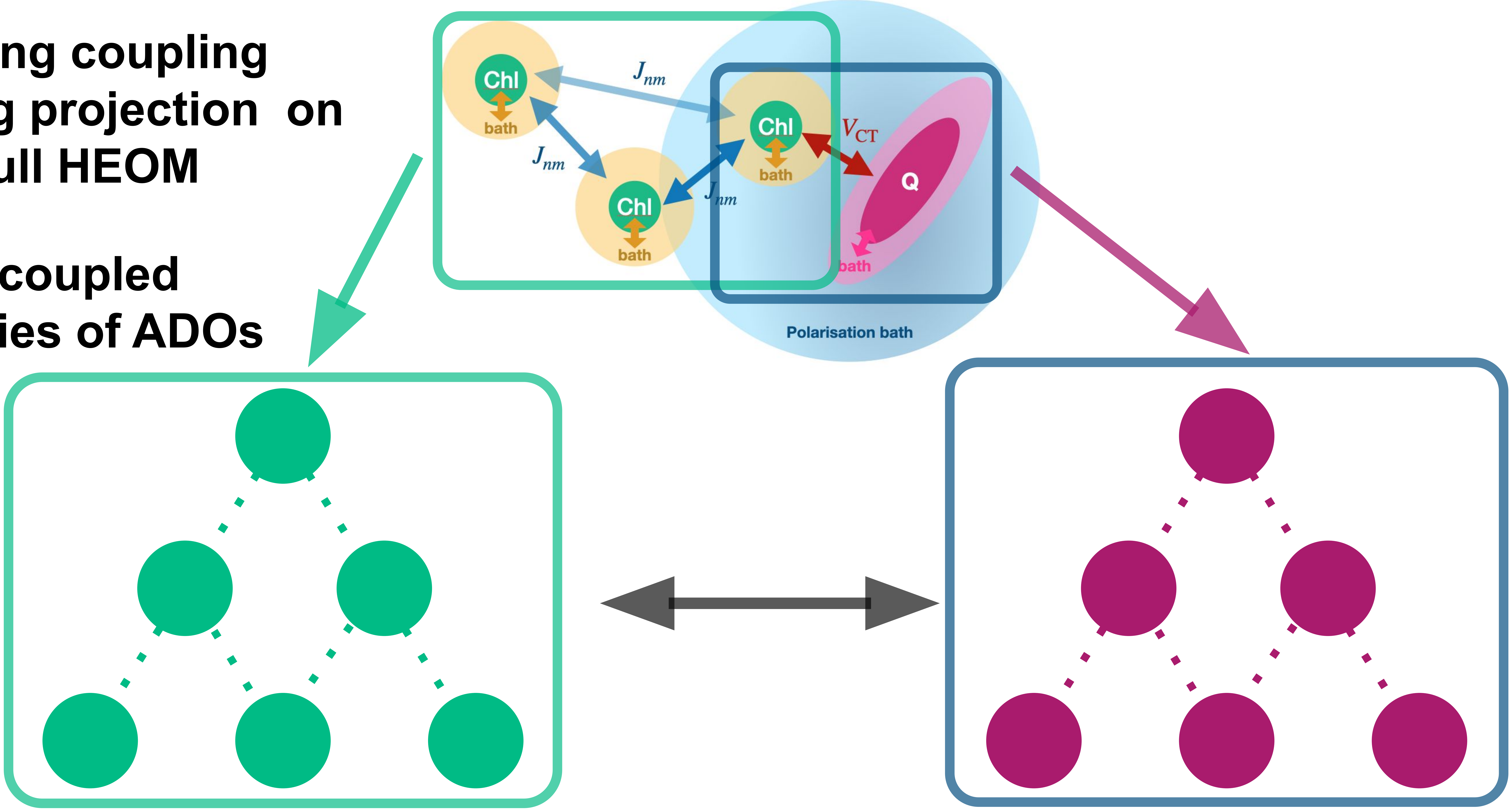
Nakajima-Zwanzig equation

Markovian approximation for kernel in the Nakajima-Zwanzig equation (*ONLY for CT processes*)

Hybrid HEOM Method

Strong coupling Zwanzig projection on full HEOM

Two coupled hierarchies of ADOs



Hybrid HEOM Method

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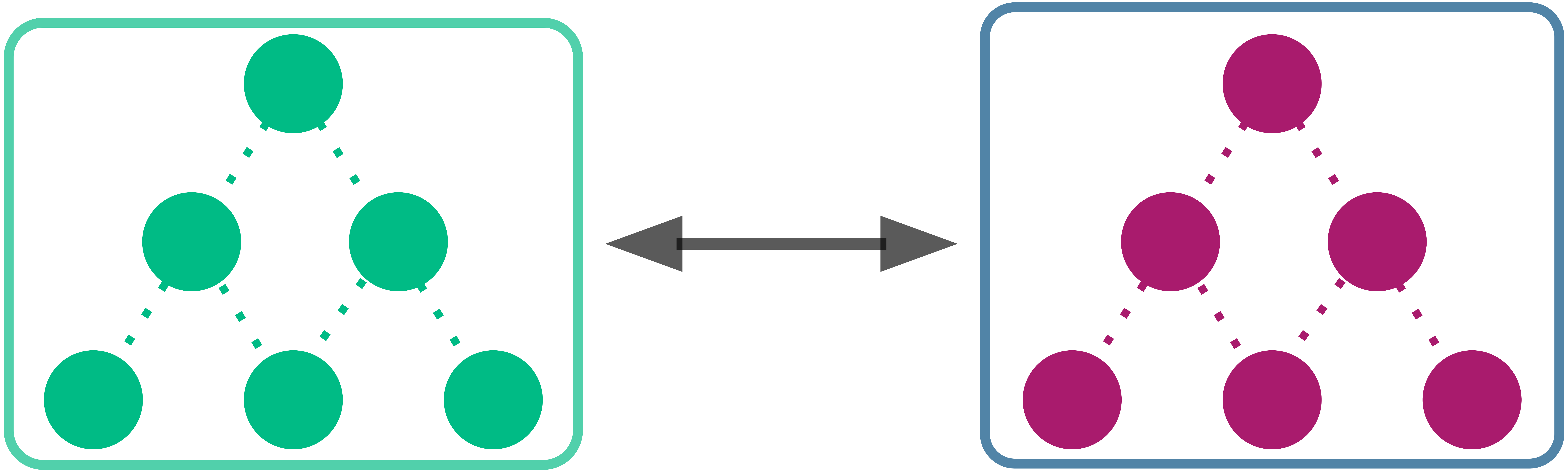
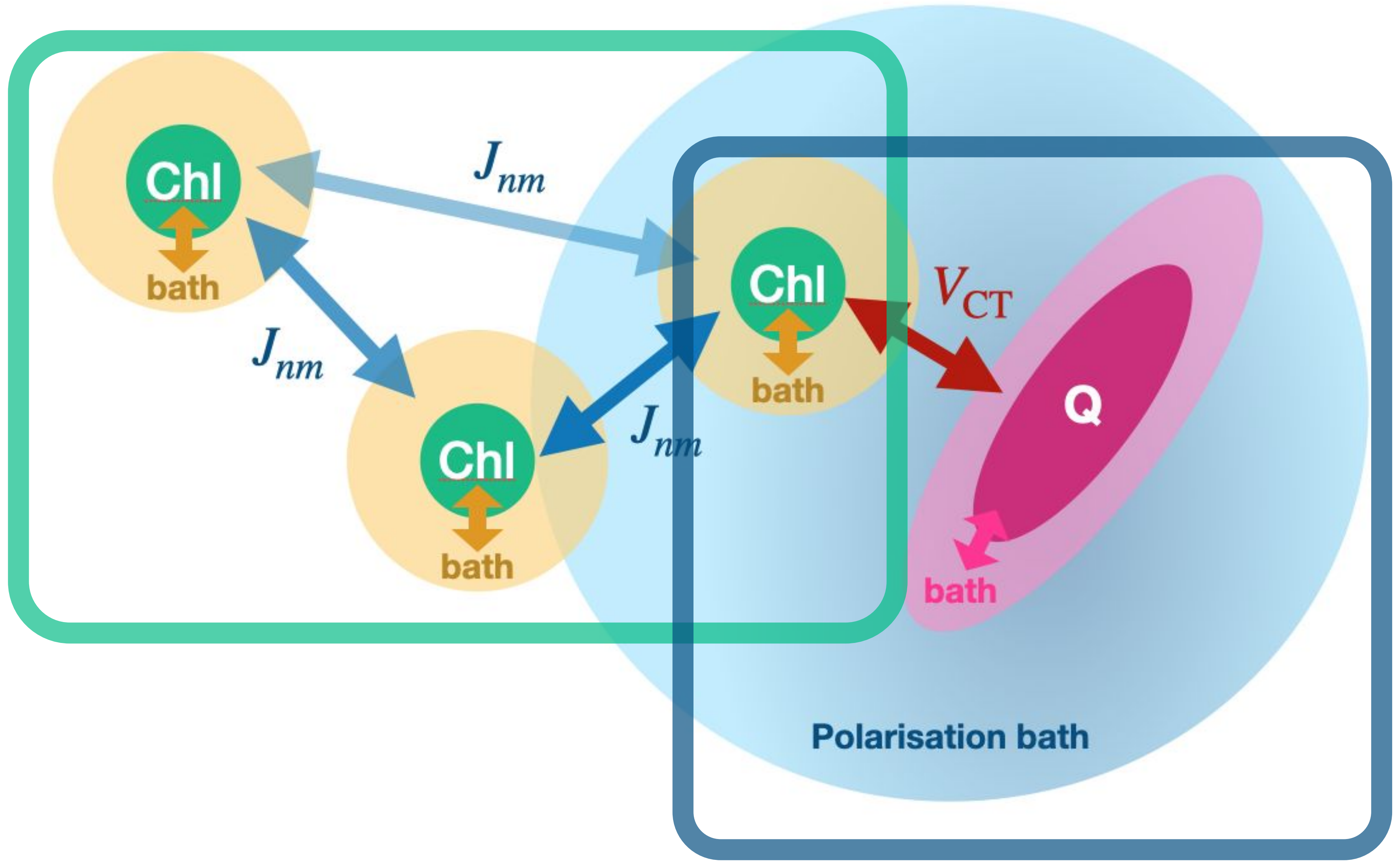


CT coupling: **selective population decay** and **perturbed exciton dynamics**

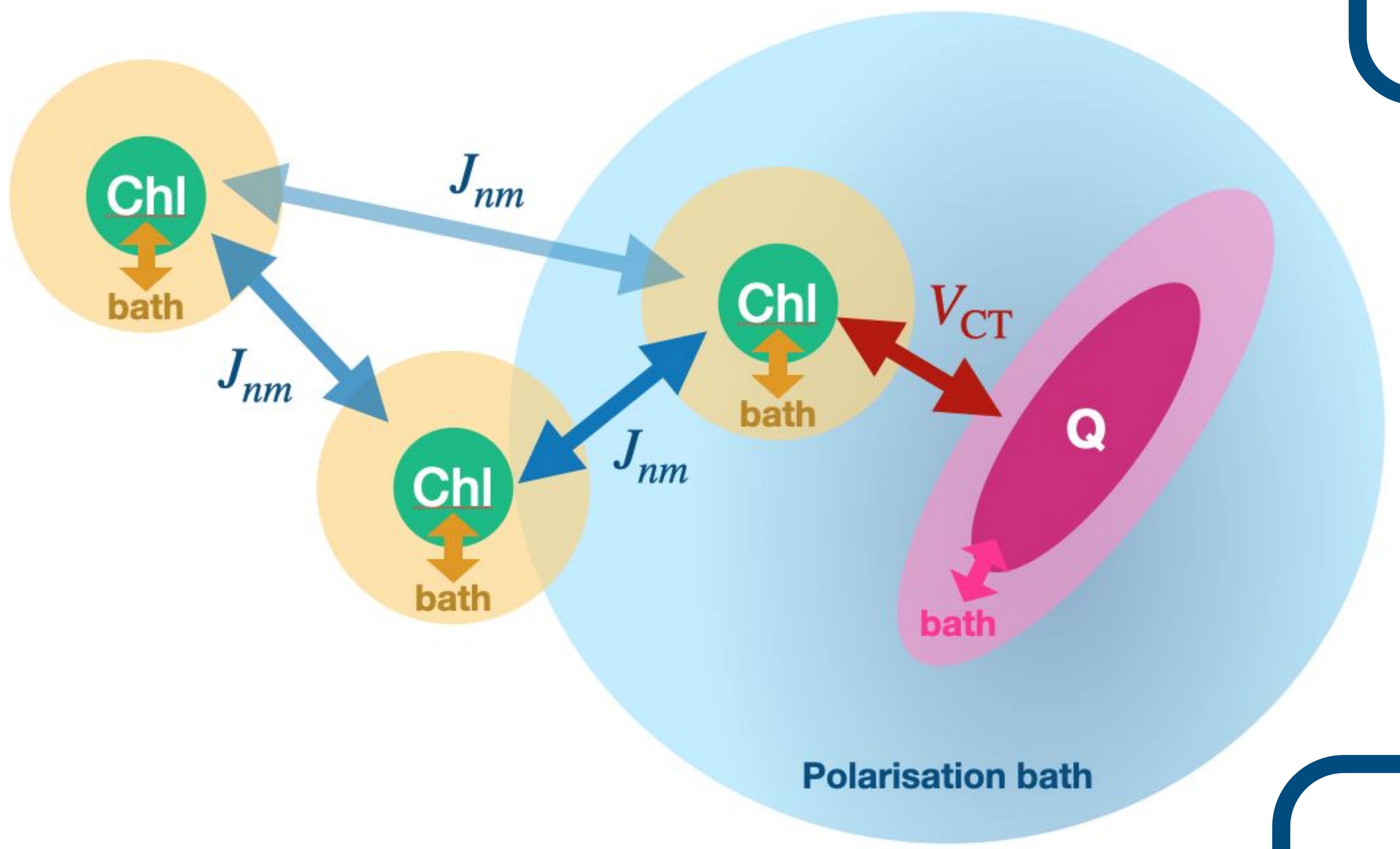
Lindblad form in certain limits

Hybrid HEOM method



Matlab code available at github.com/tomfay/heom-lab

Hybrid HEOM method



Complete set of auxiliary density operators

Project out strongly coupled baths

Perturbation theory expansion of Nakajima-Zwanzig kernel

Technical aside

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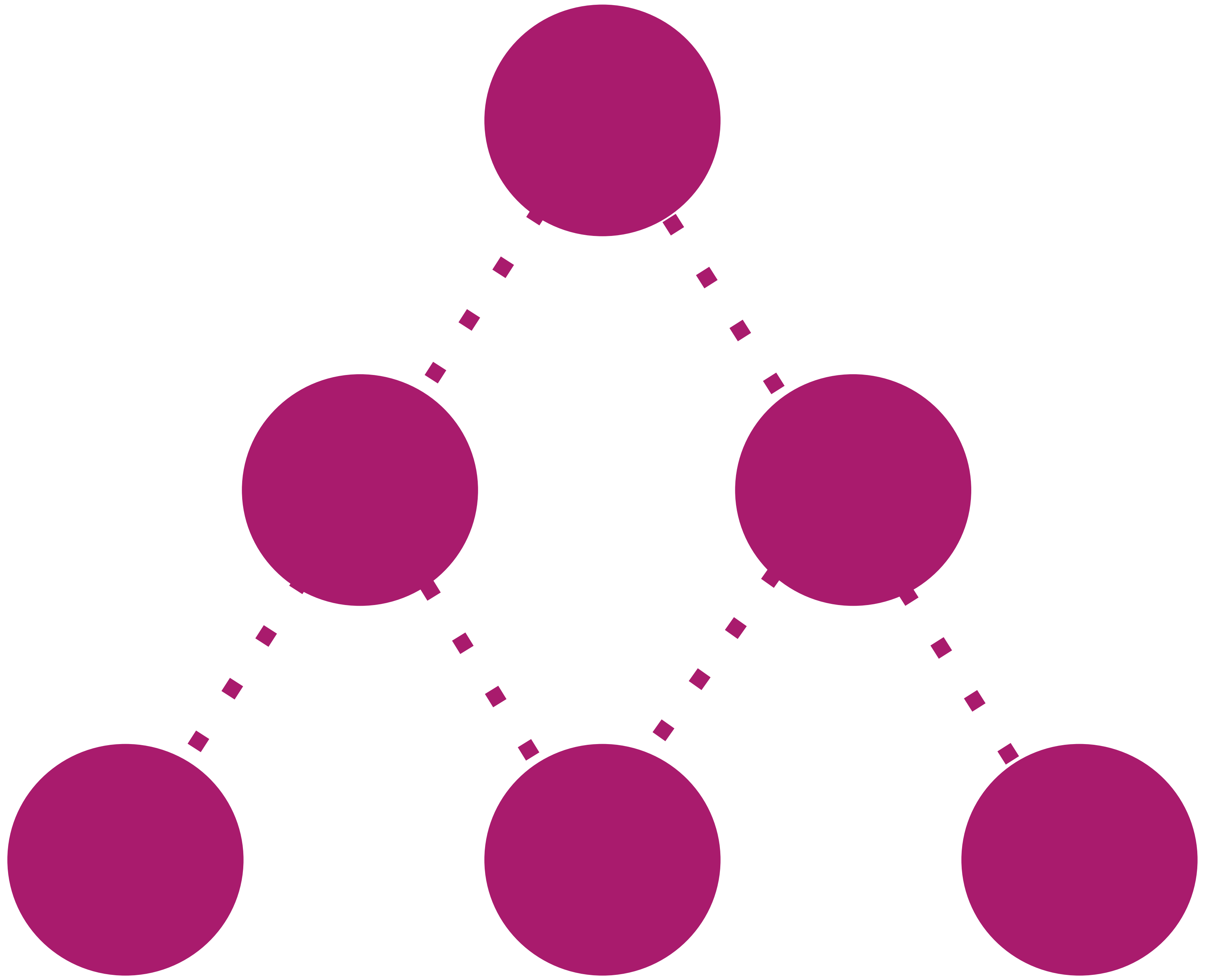
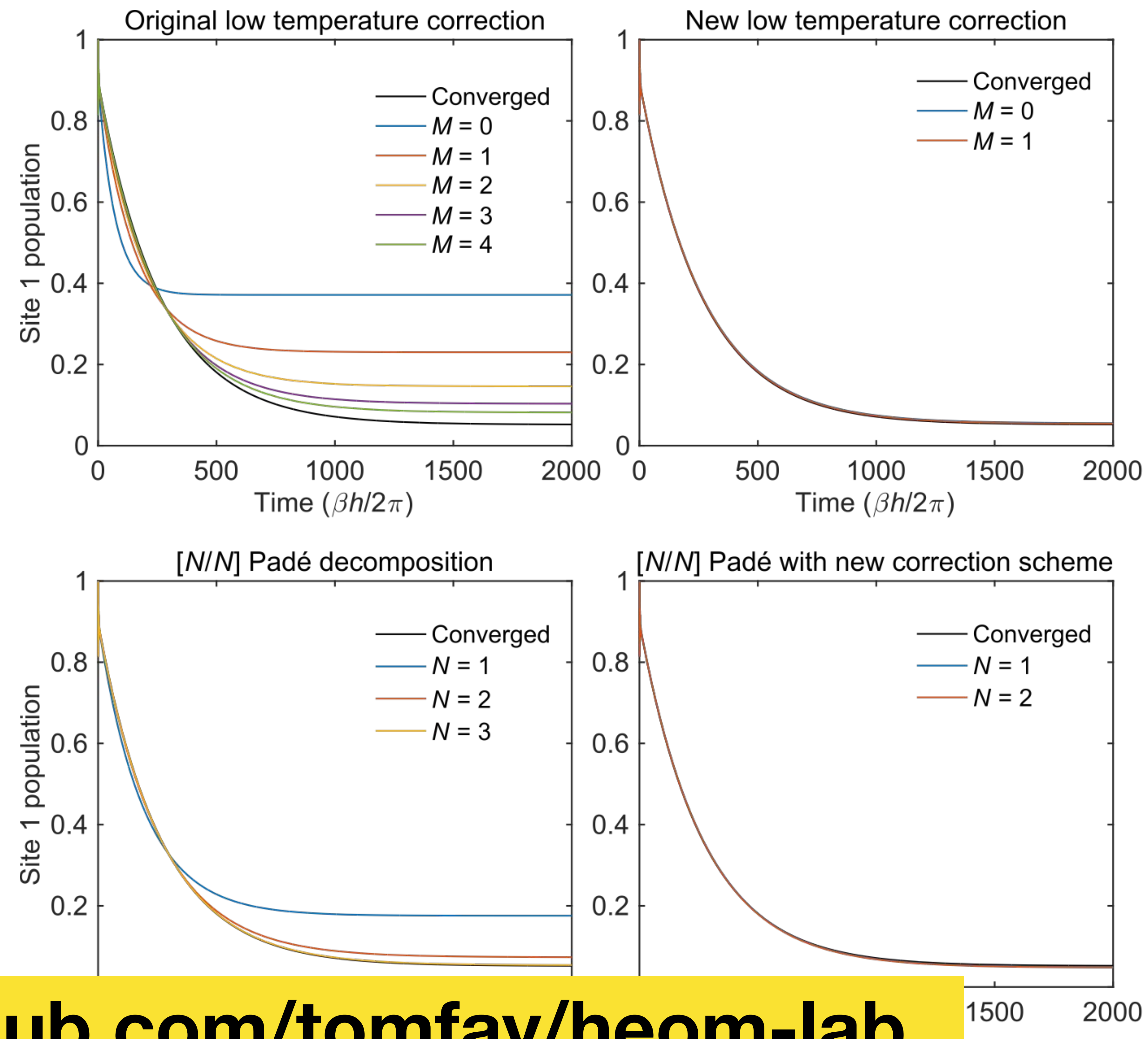
Efficient **propagation** and **truncation** of HEOM



New **low temperature correction** + specialised **propagation algorithm**

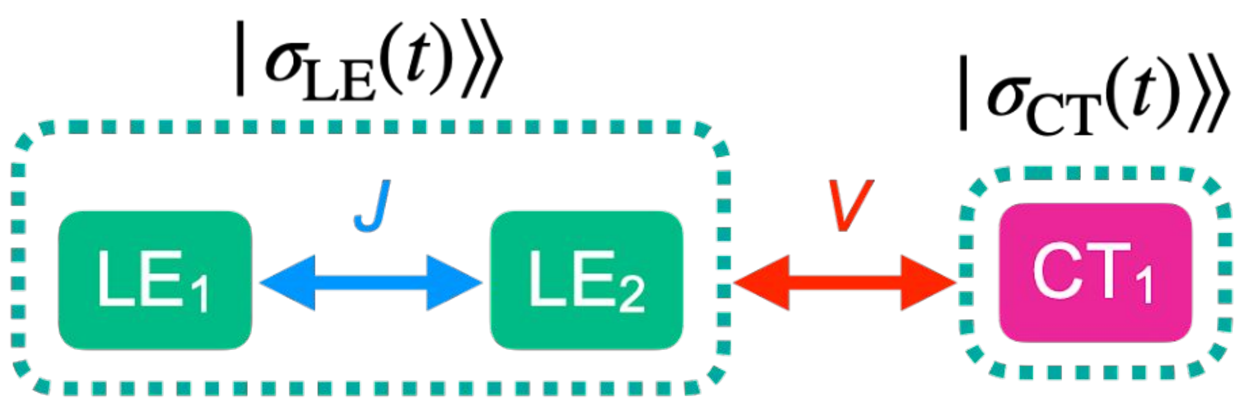


Matlab code available at <u>github.com/tomfay/heom-lab</u>

TPF, A simple improved low temperature correction for the hierarchical equations of motion. *J. Chem. Phys.* 014101, (2022).

Hybrid HEOM method

A



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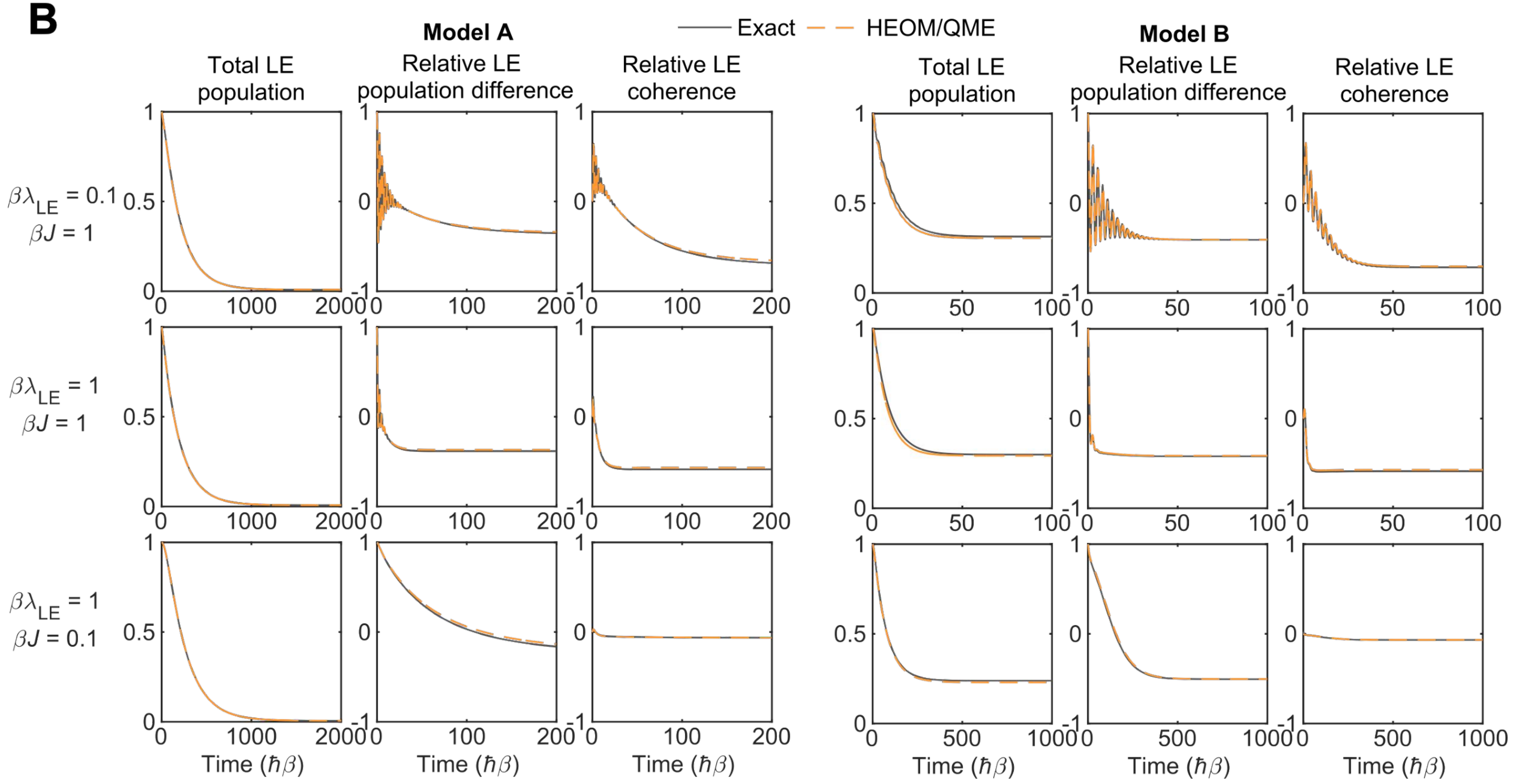

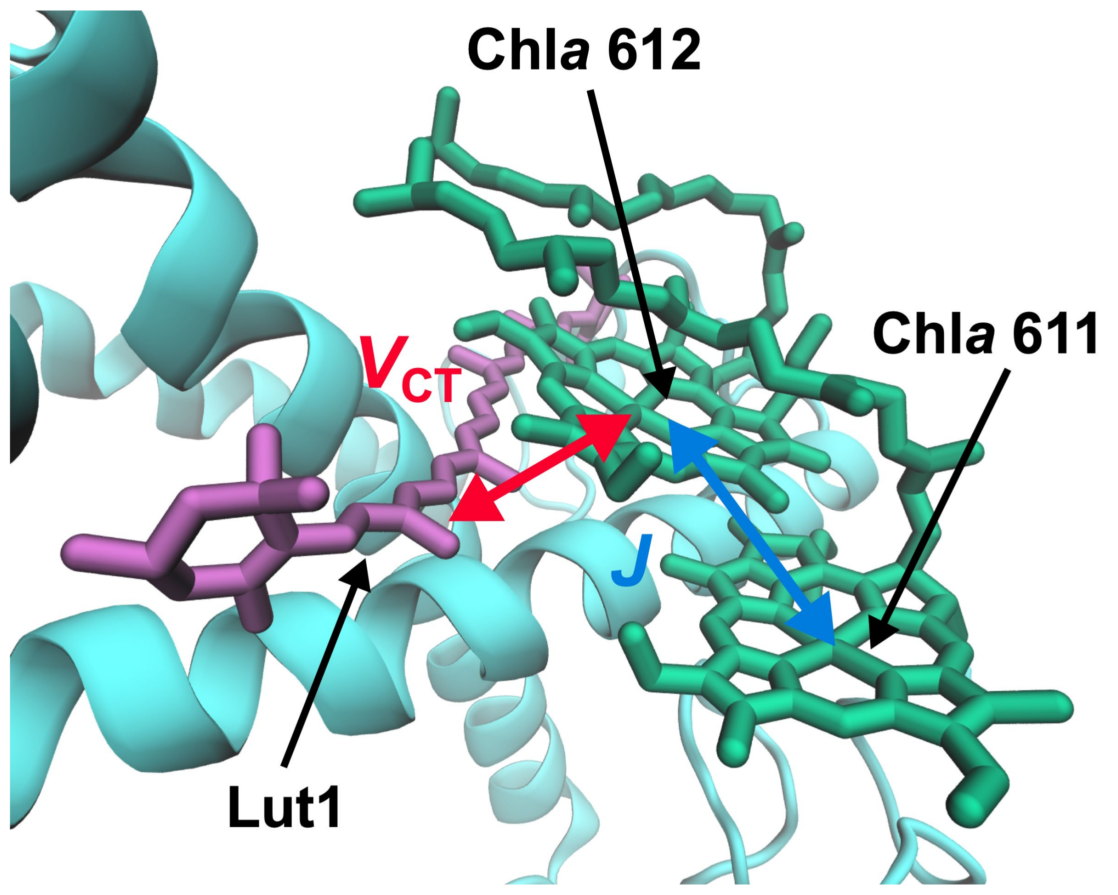

Benchmark results for a **dimer of Chl** coupled to a **CT quencher**

Exciton quenching in LHCII

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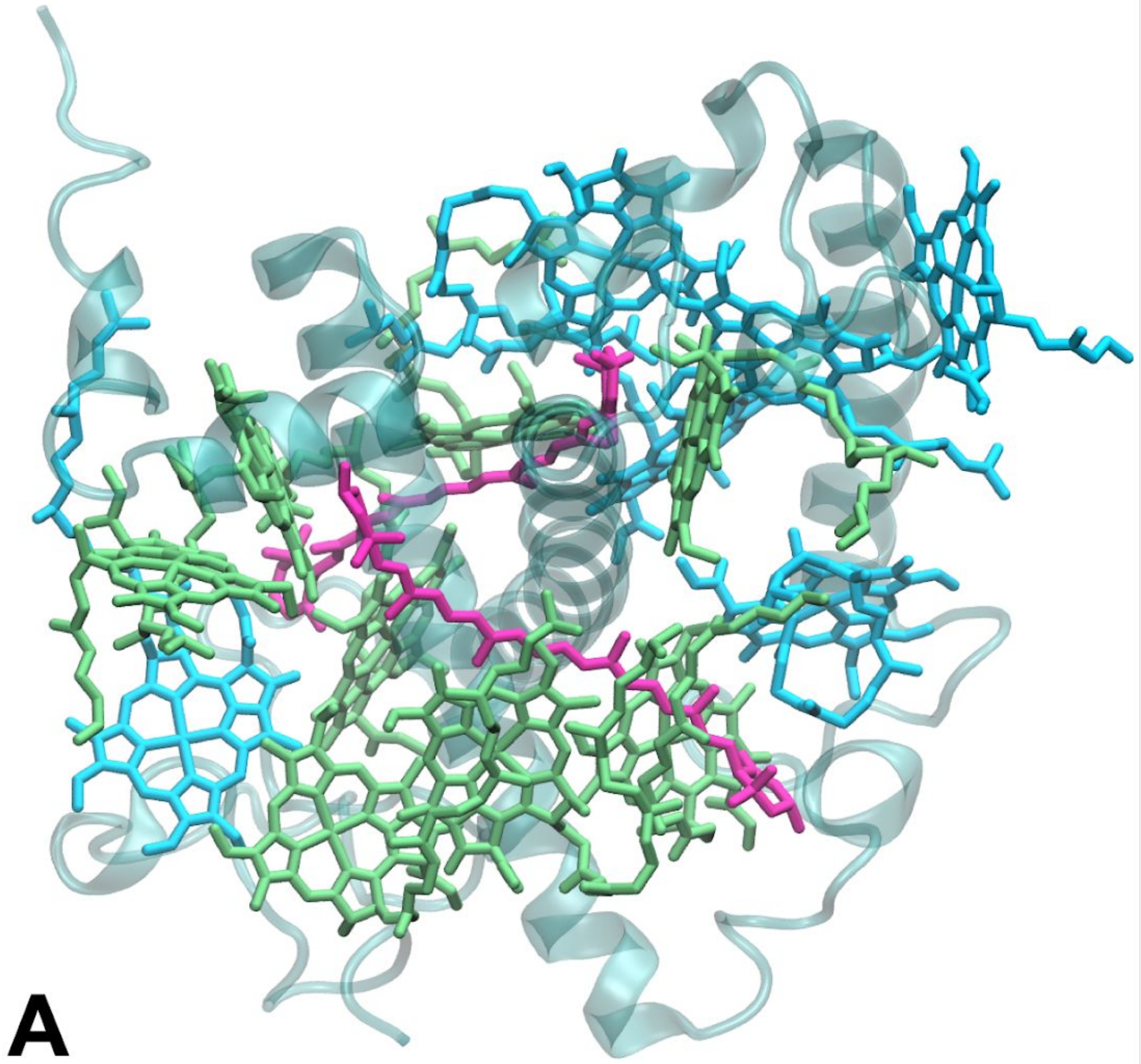
How do **exciton dynamics** affect **CT quenching** in **LHCII**?

Exciton quenching in LHCII

Multiple coupled Chl*a* and Chl*b*

Radiative +NR + CT decay pathways



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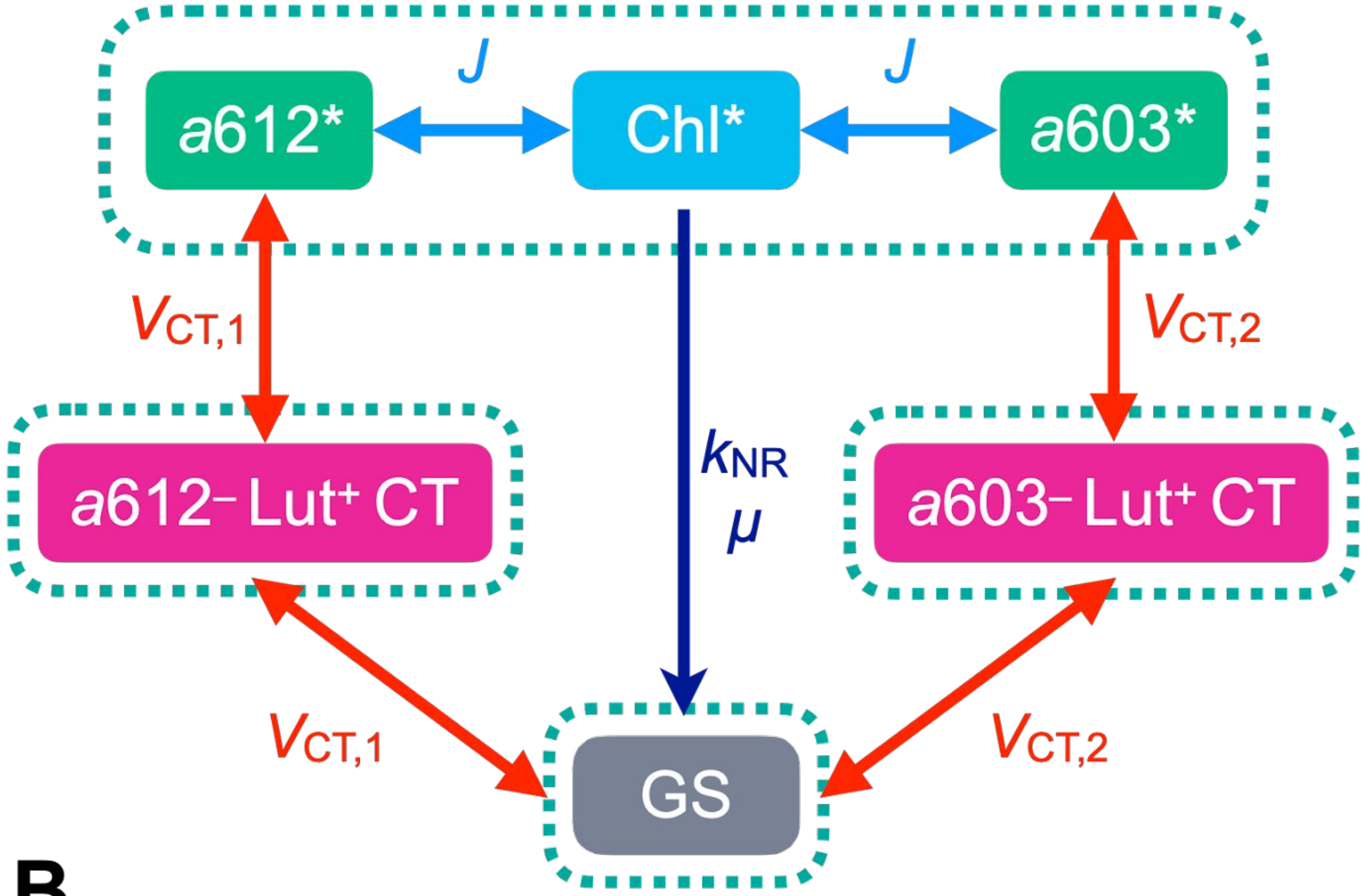

B

Cupellini, L., Calvani, D., Jacquemin, D. & Mennucci, B. *Nat. Commun.* **11**, 662 (2020).

Exciton quenching in LHCII

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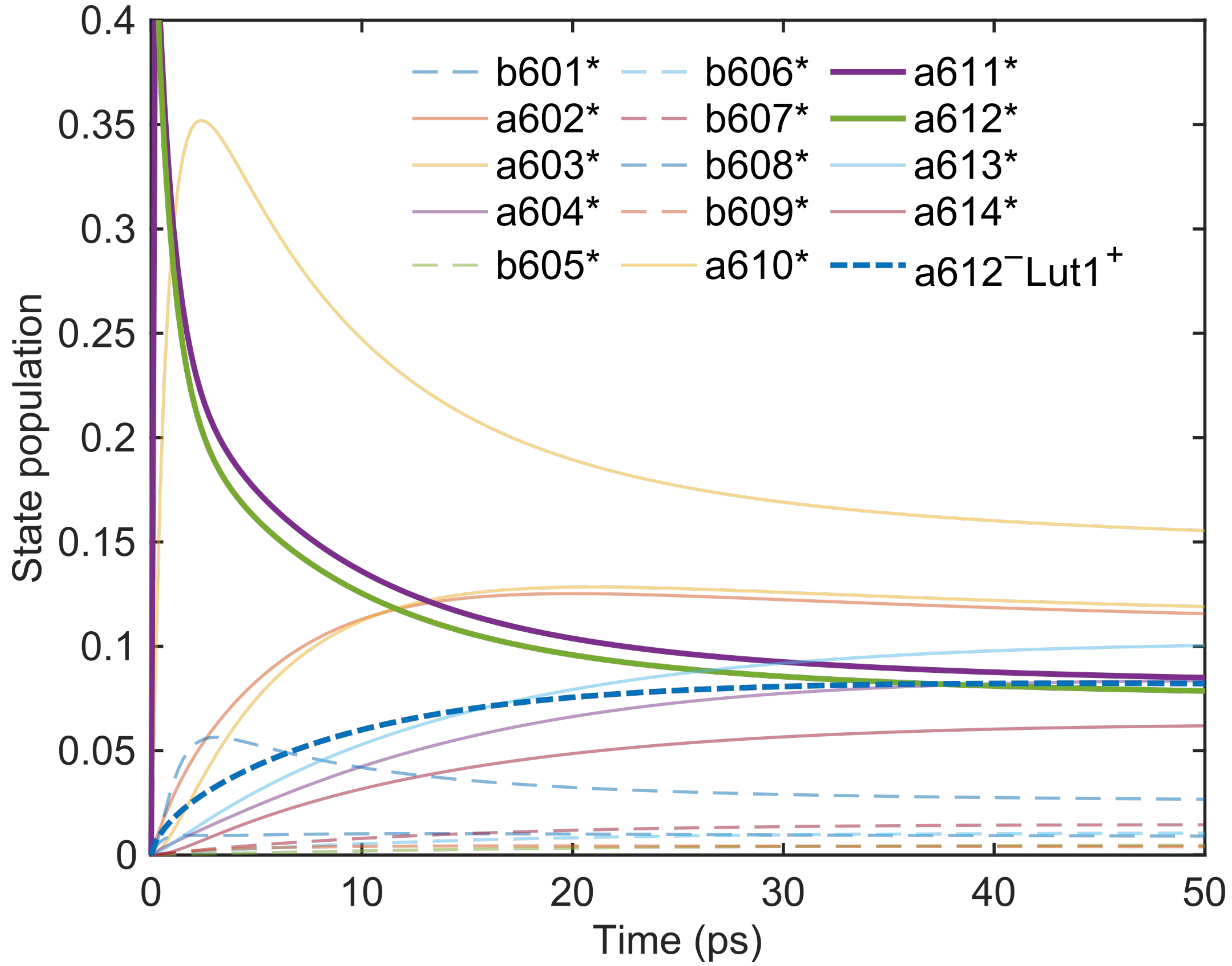
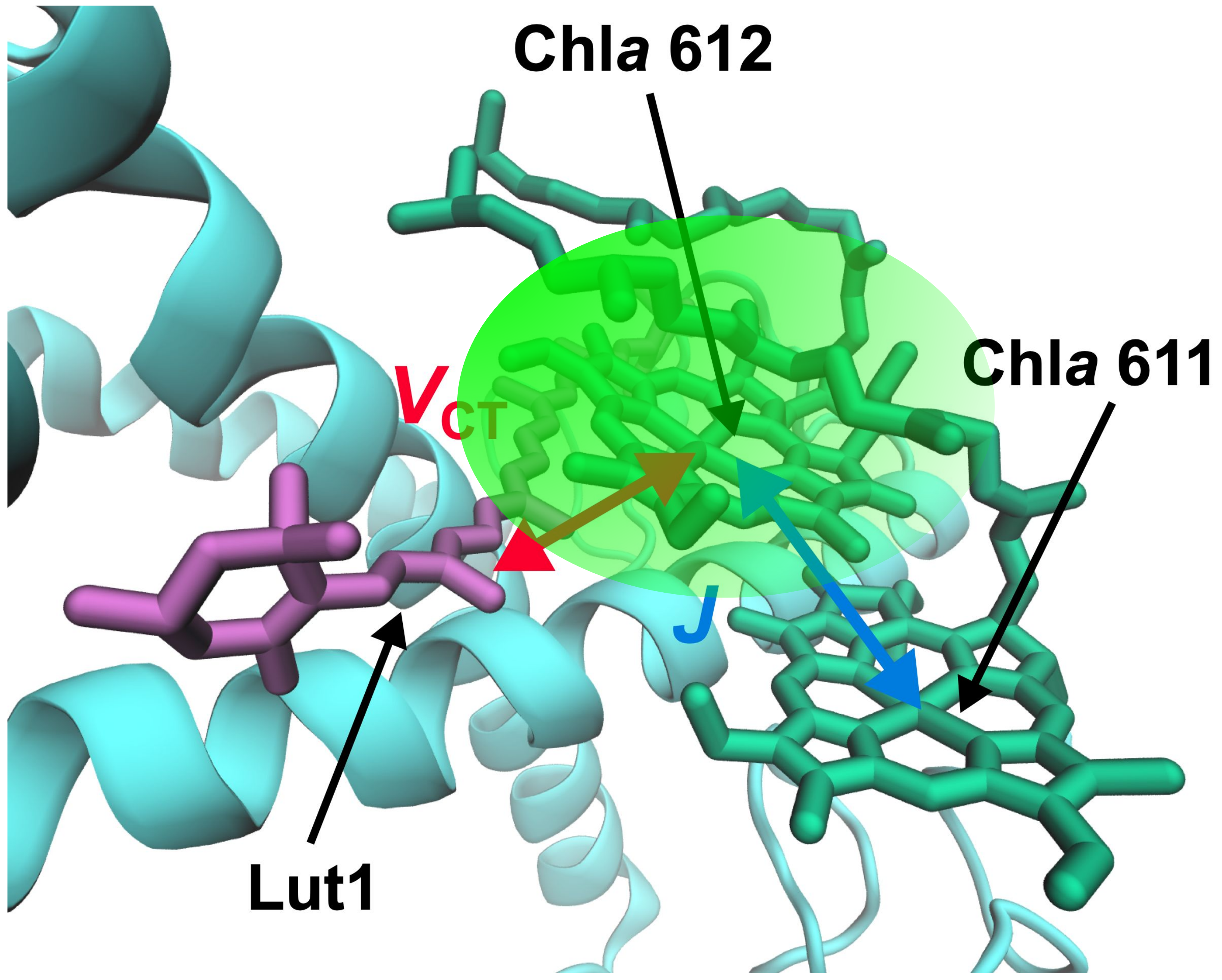
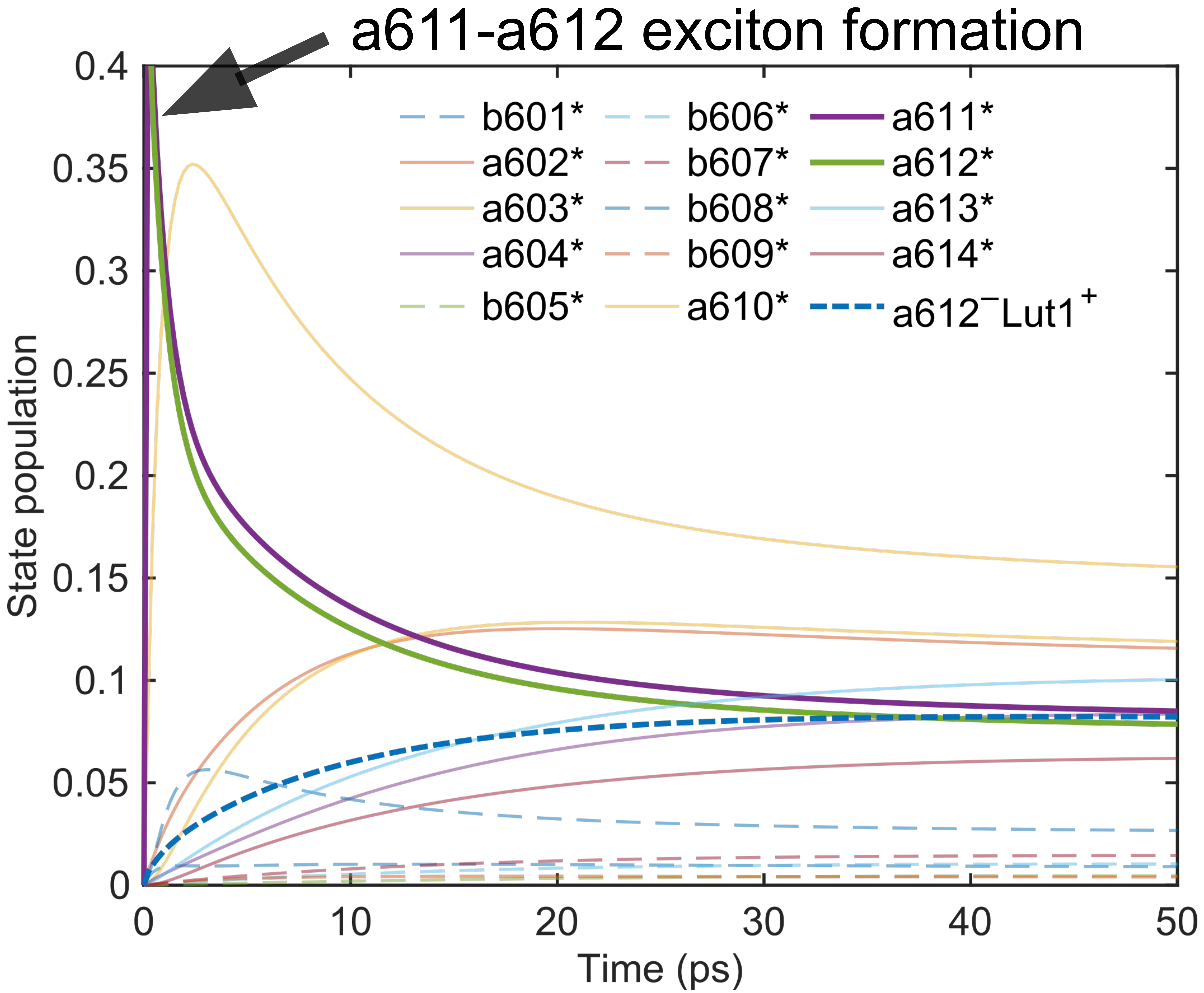
Populations of different chlorophyll (LE) excited states



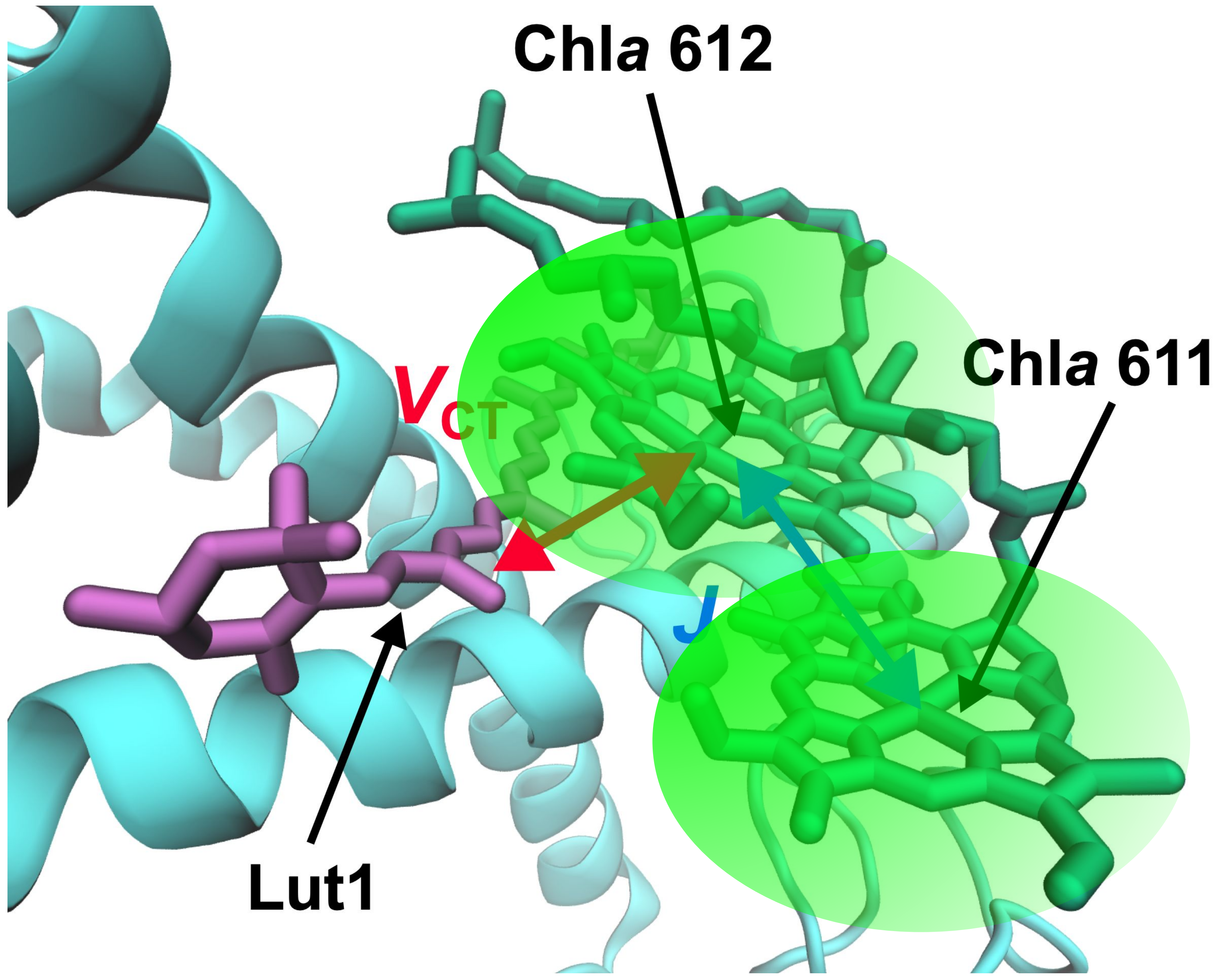
Initial excitation on a612



Exciton quenching in LHCII



Quantum coherence between a611/a612 excitations



Exciton quenching in LHCII

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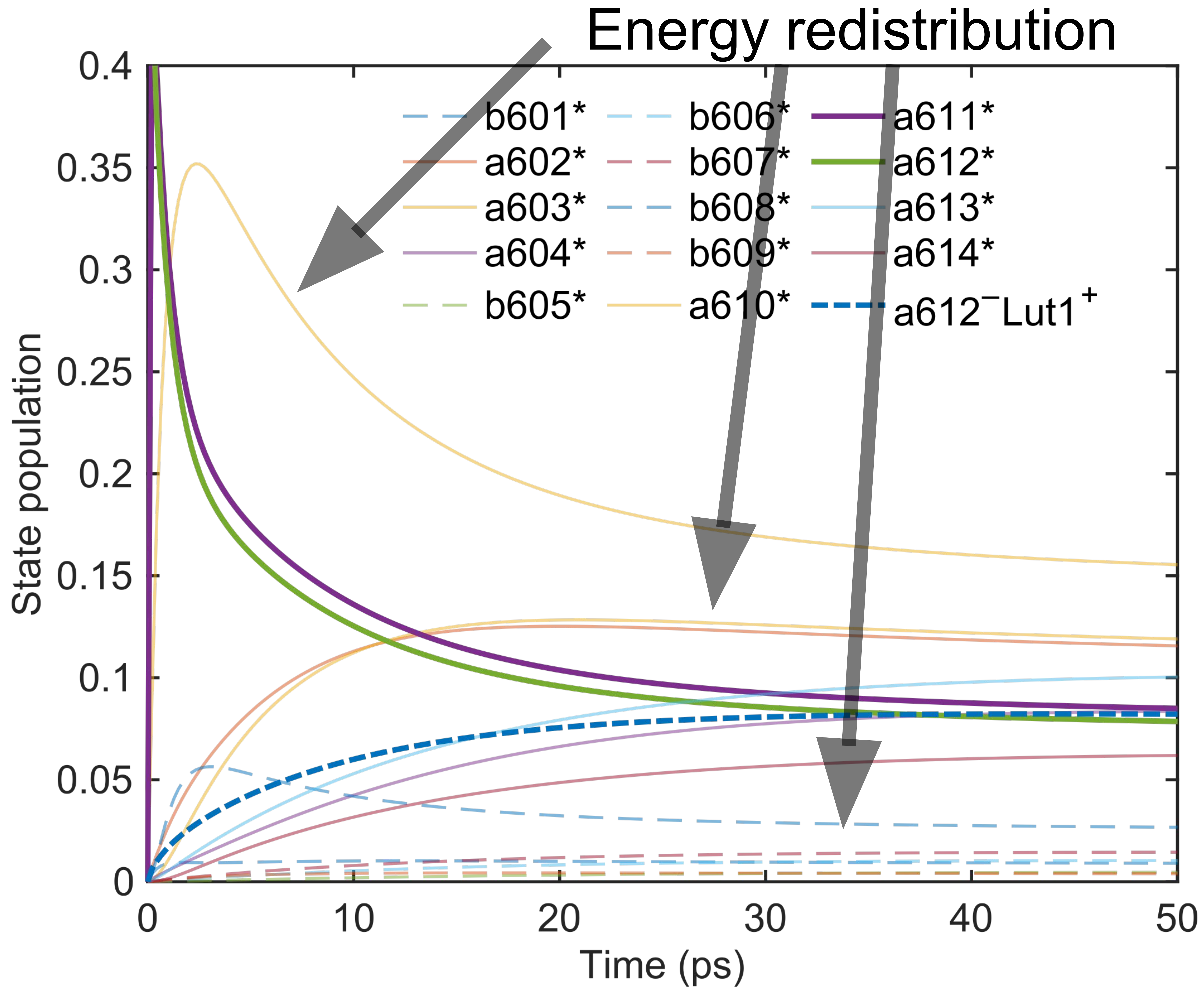
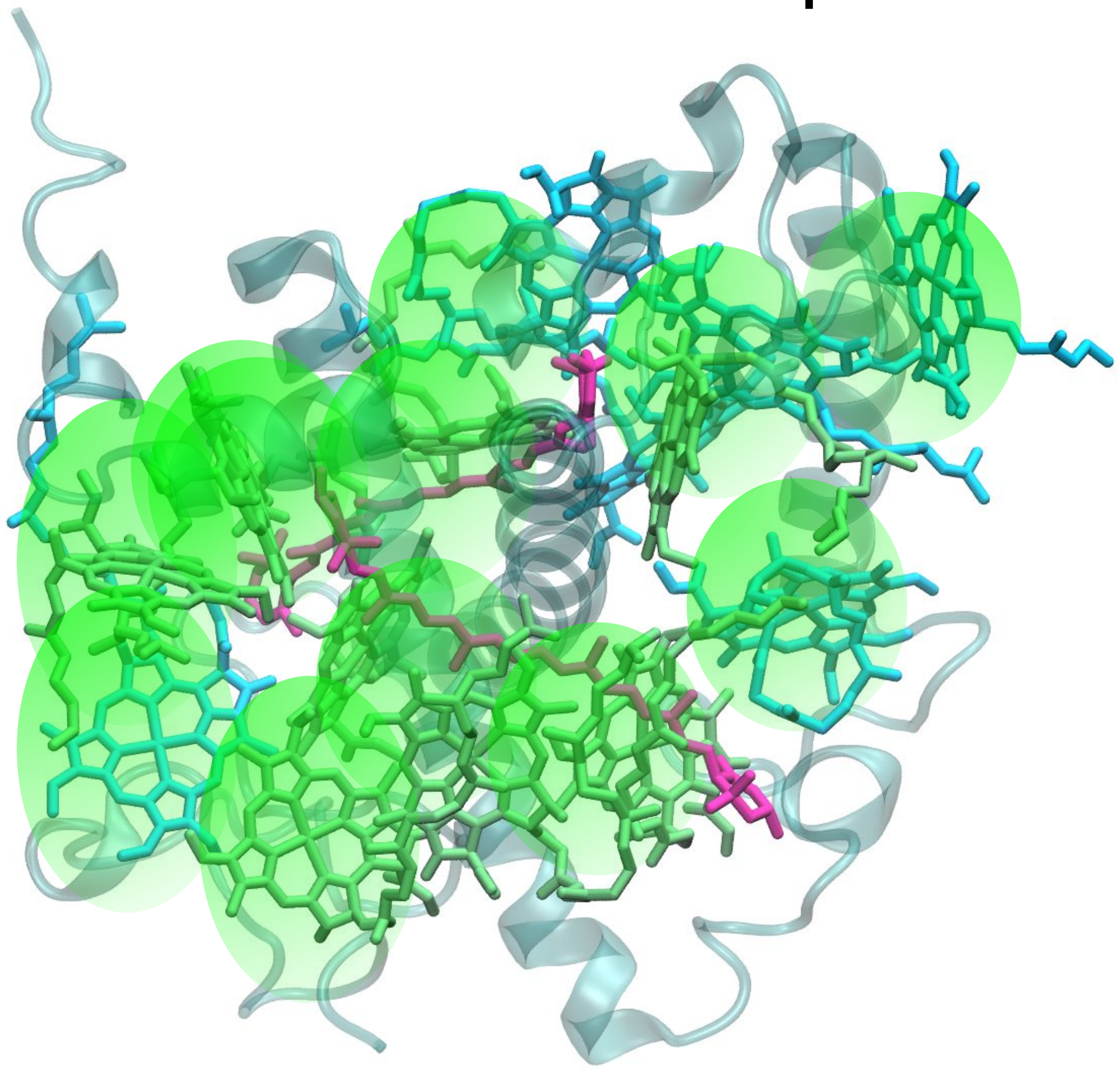


Mixture of coherent and incoherent transport



Exciton quenching in LHCII

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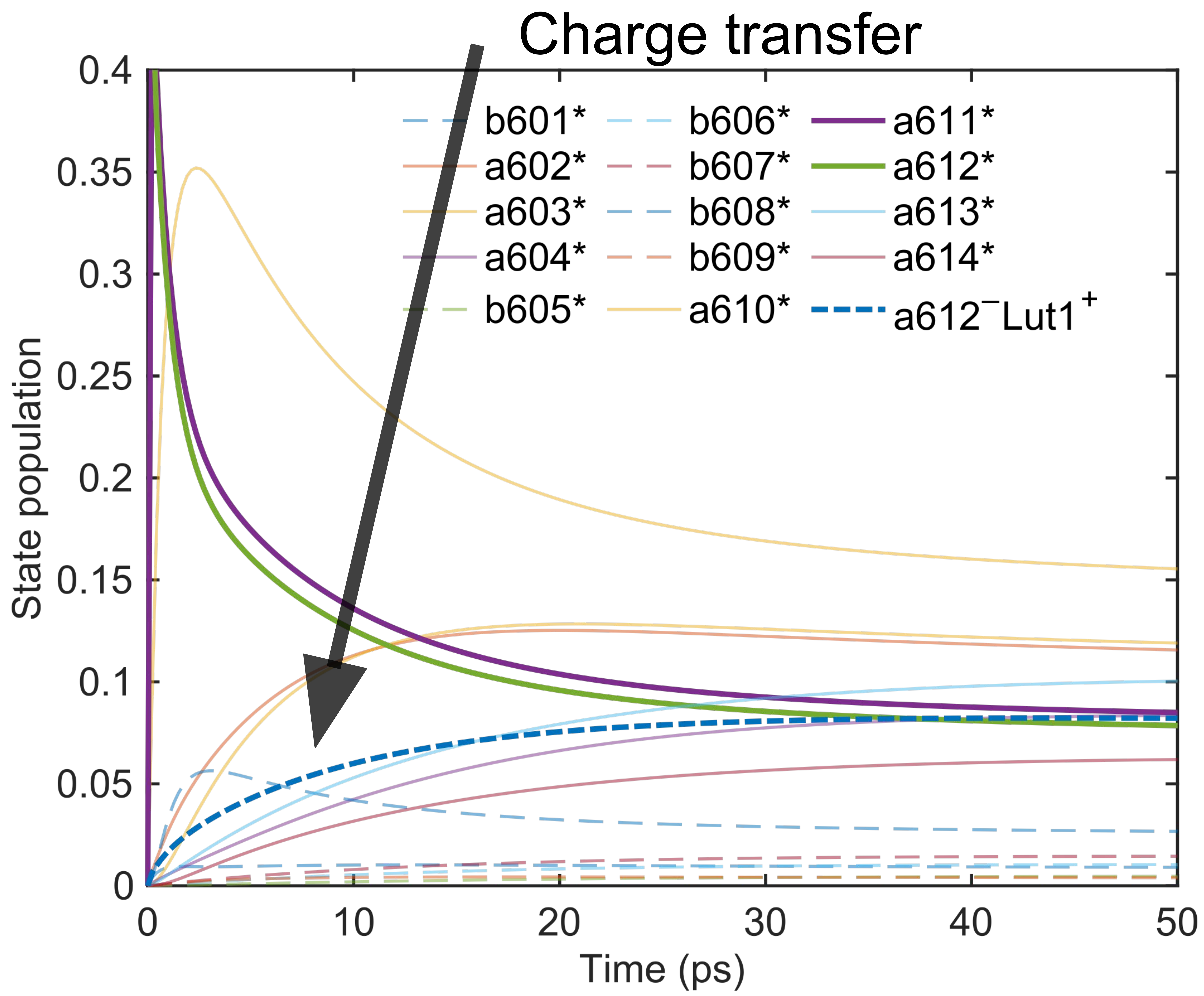
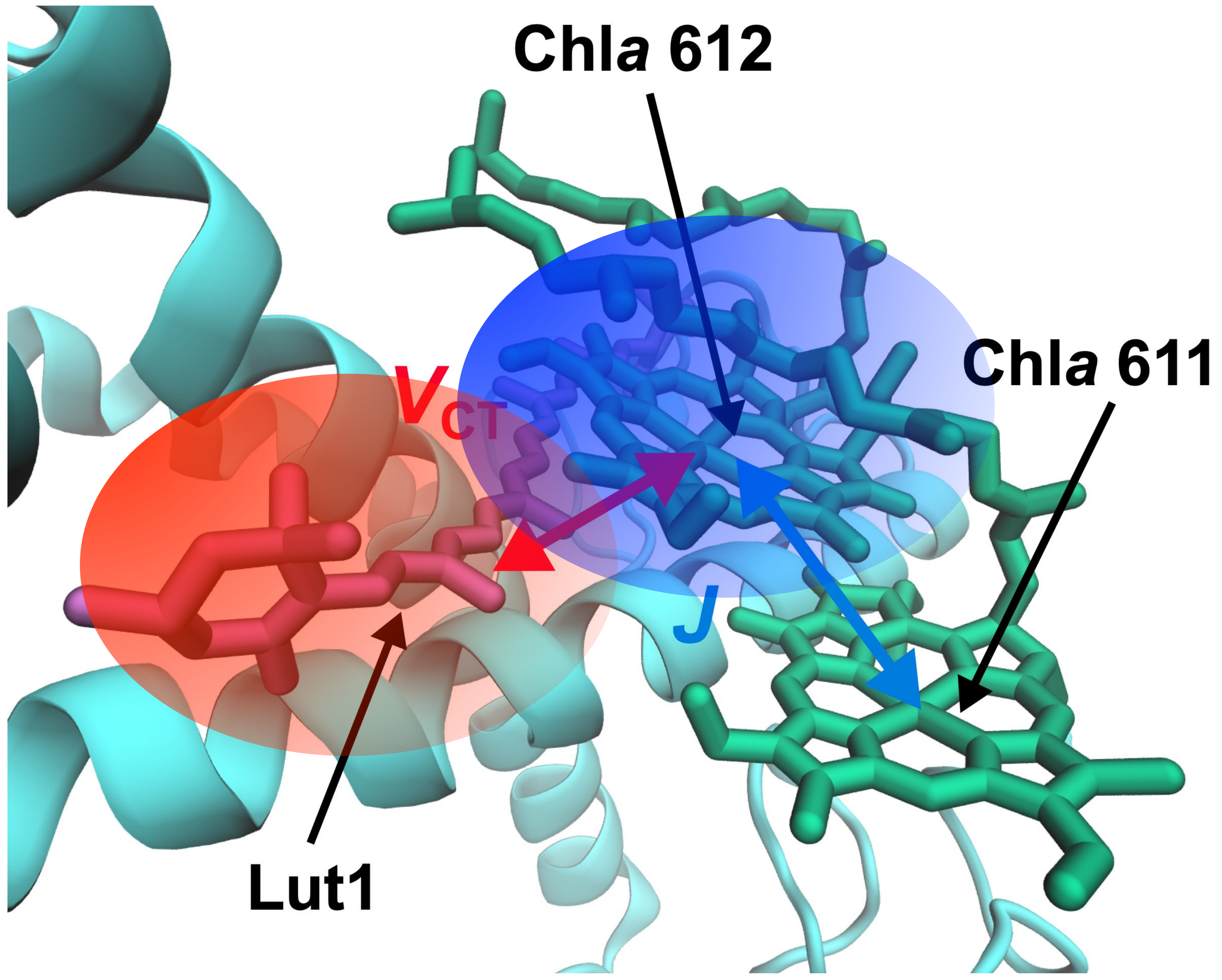
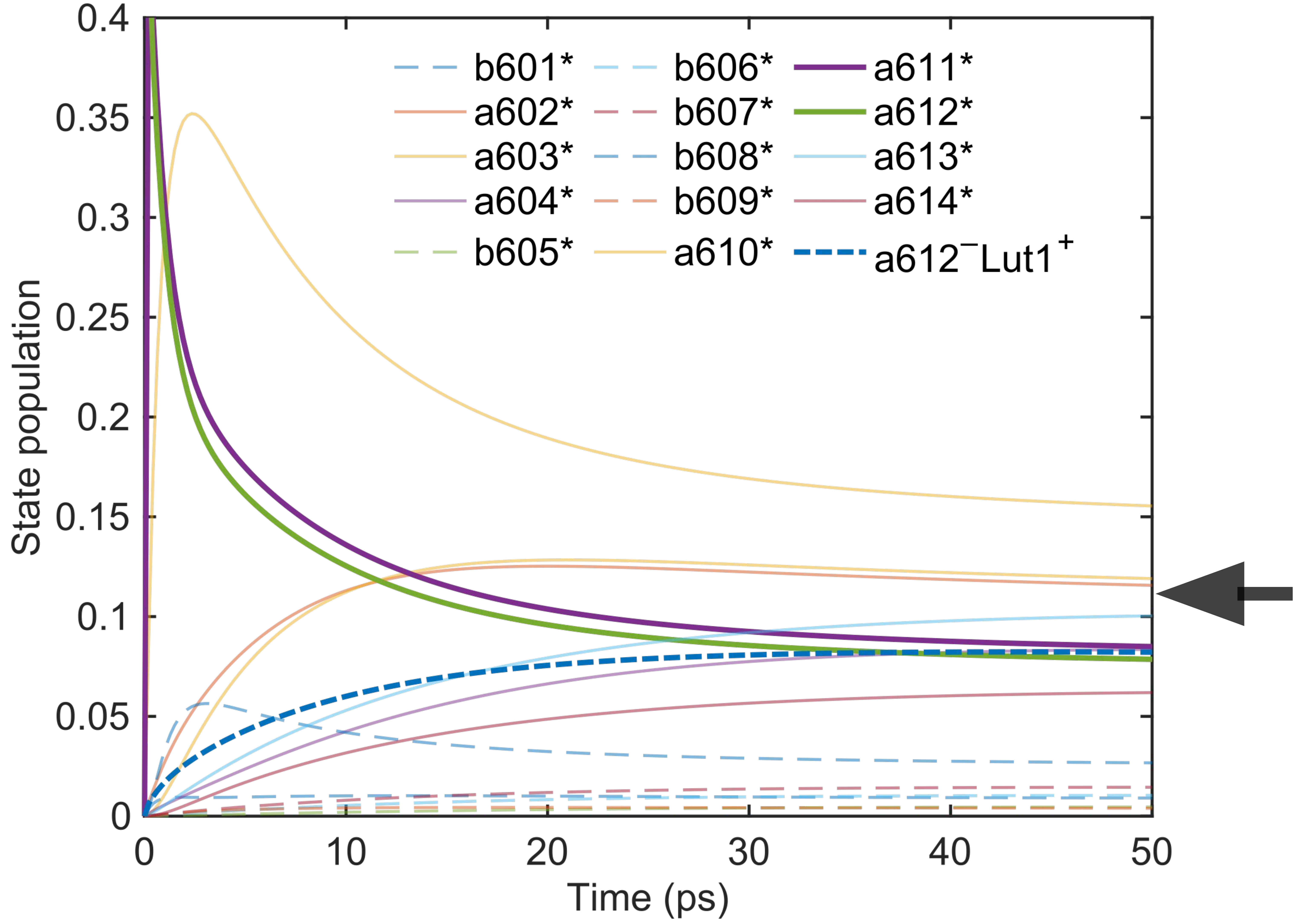




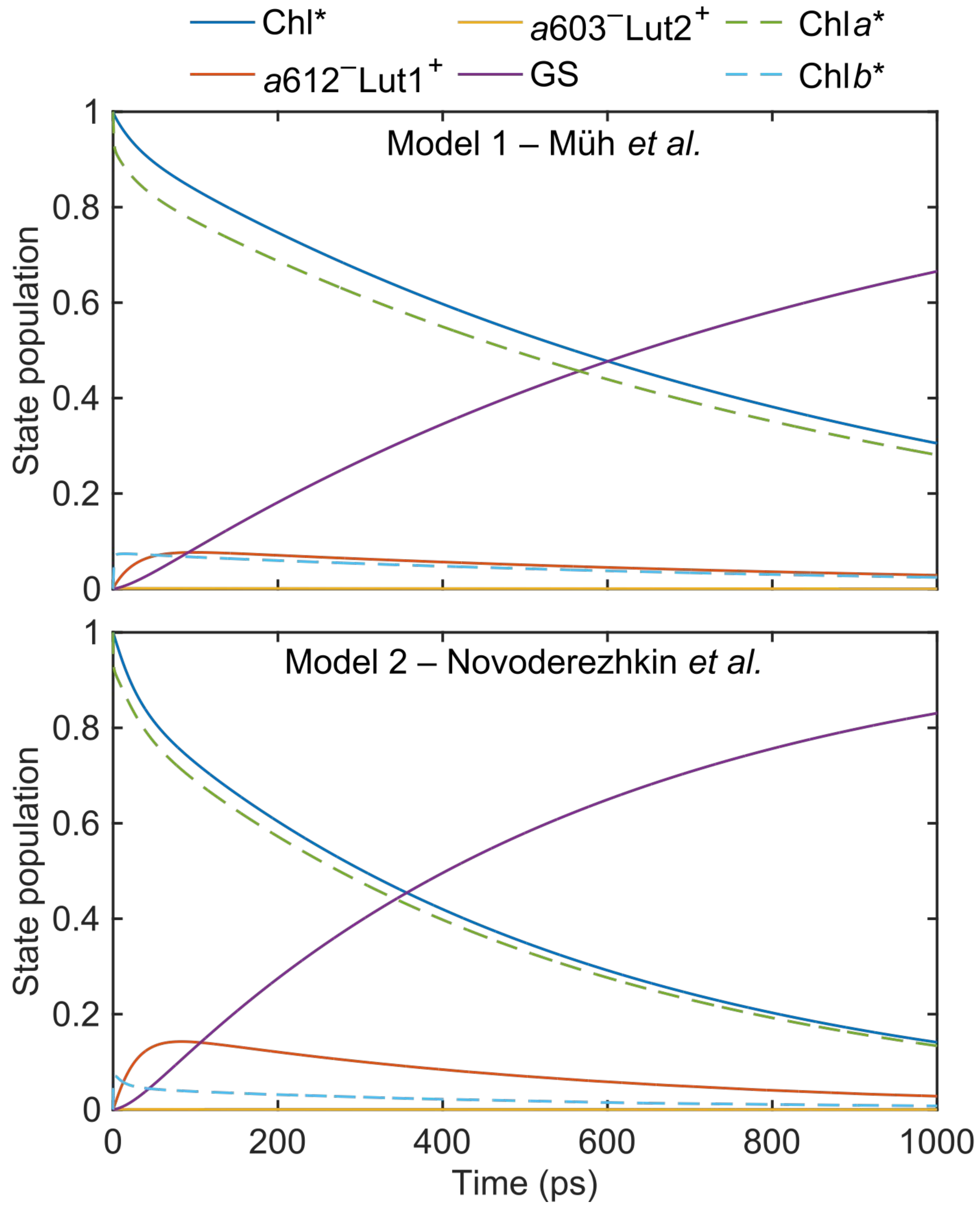
Exciton quenching in LHCII



Exciton formation between a611 and a612 **diminishes CT quenching**

CT population without a611-a612 exciton formation

Exciton quenching in LHCII



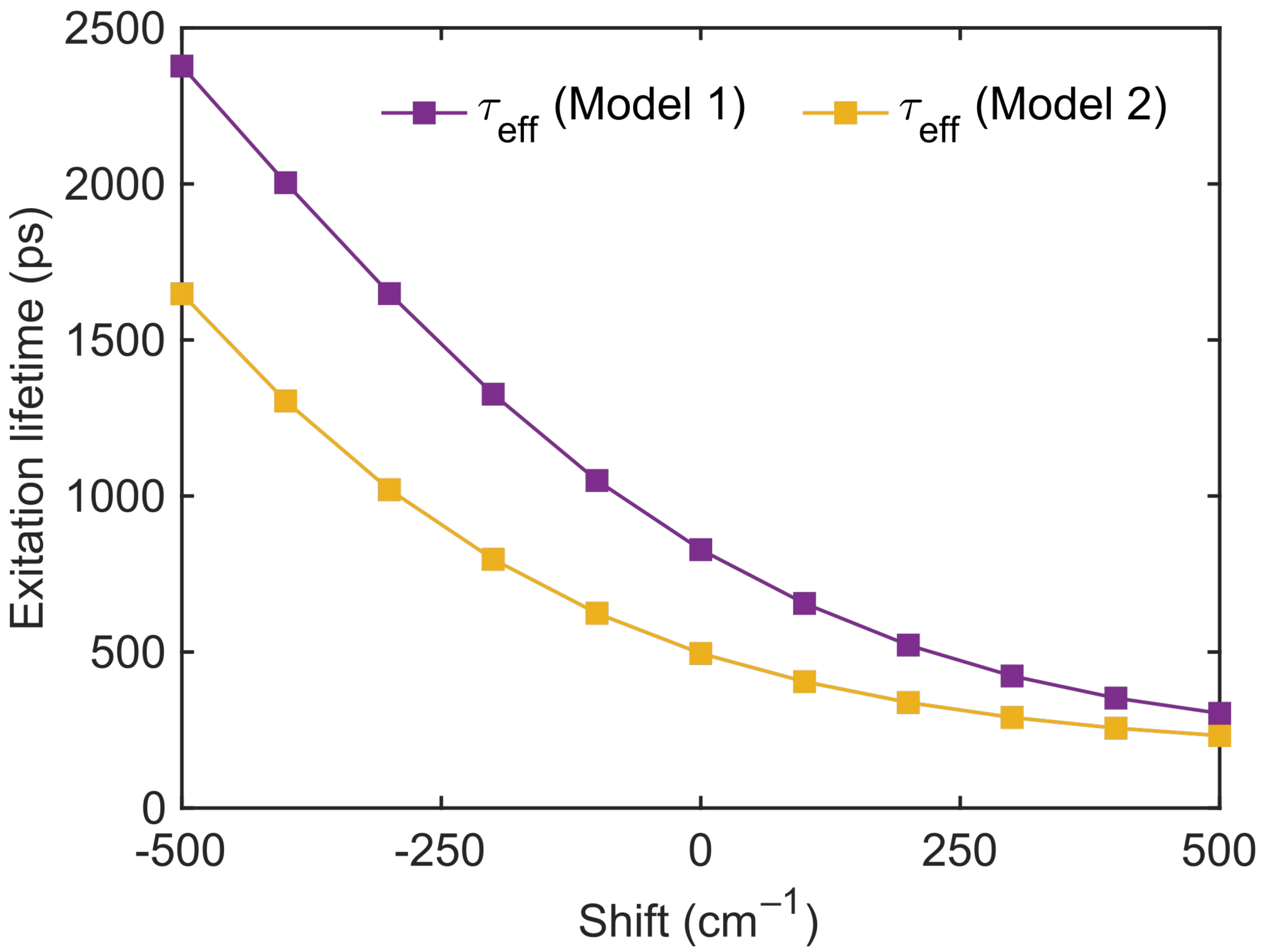
Different exciton Hamiltonians for LHCII predict **different excitation lifetimes**

Arises due to **different energies of a611/a612** excitations

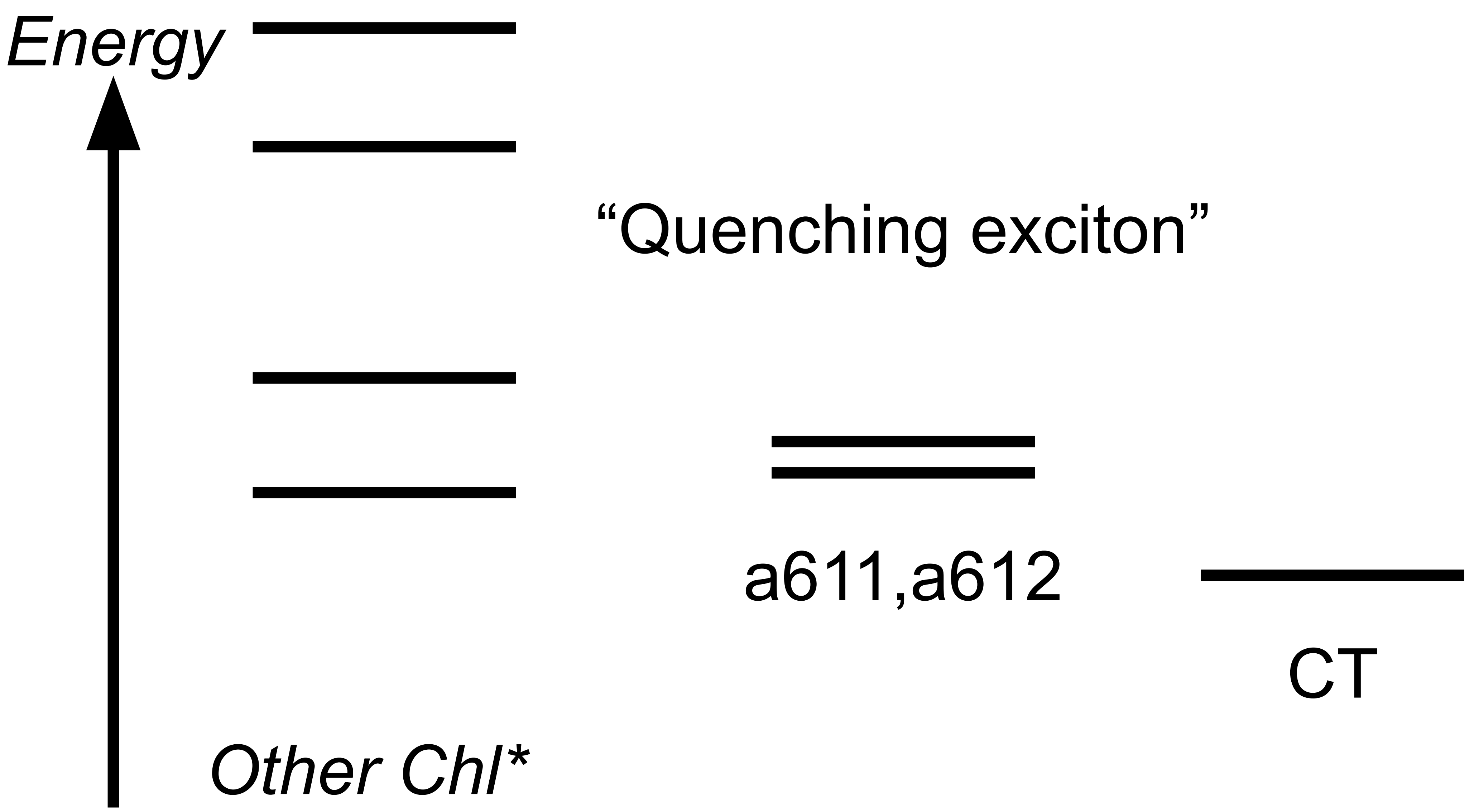
(No quantum coherence)

Comparison to QUAPI, ACE, TEMPO…?

Exciton quenching in LHCII



Shifting a611/a612 energies relative to other LE states has a **large affect on exciton lifetime**



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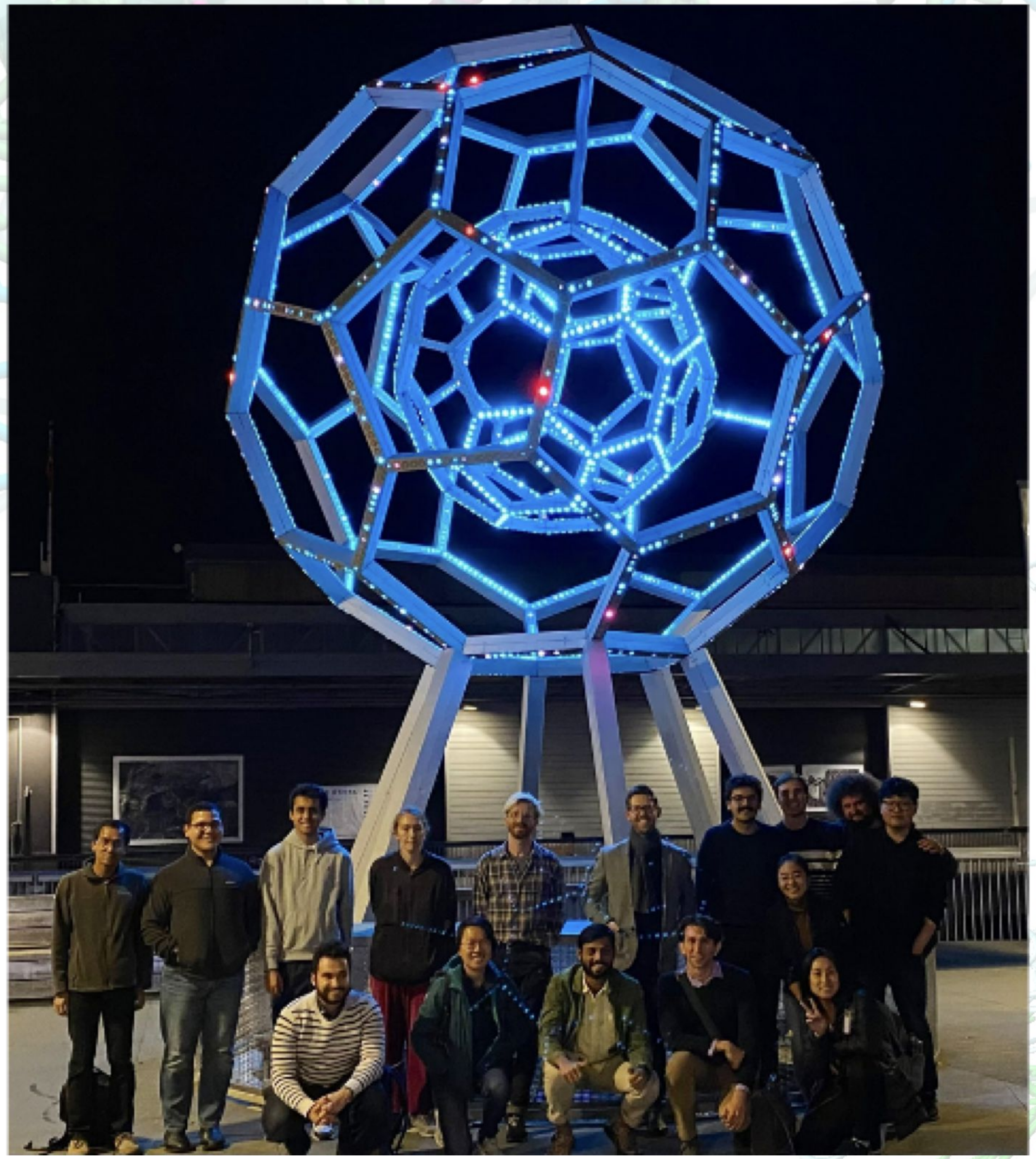

Thank you for listening!

Thanks to:
David Limmer & the Limmer Lab, Audrey Short & Graham Fleming

Funding: