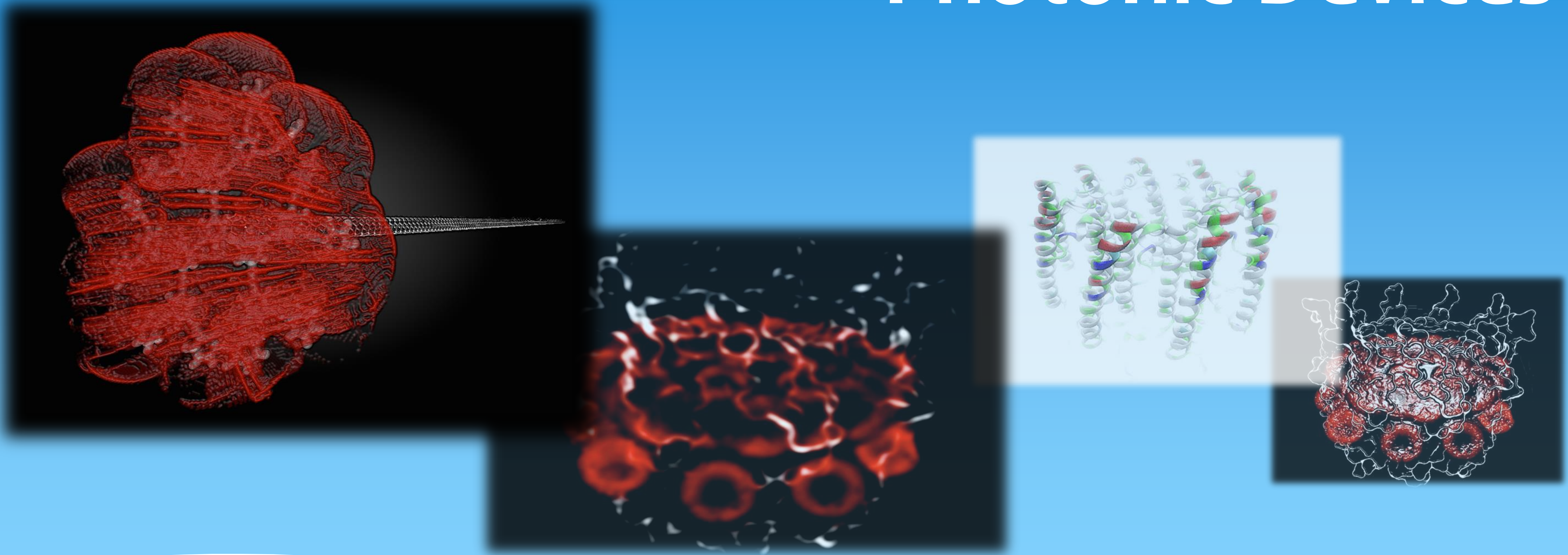
Data-driven Design of Quantum Photonic Devices



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Stanford University
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Why light-driven devices?

Molecular response on the order of *femtoseconds*
Spatial dimensions on the order of *nanometers*

The Age of Metamaterials

- Tunable optical properties
- Specific light-activated mechanisms

Information processing

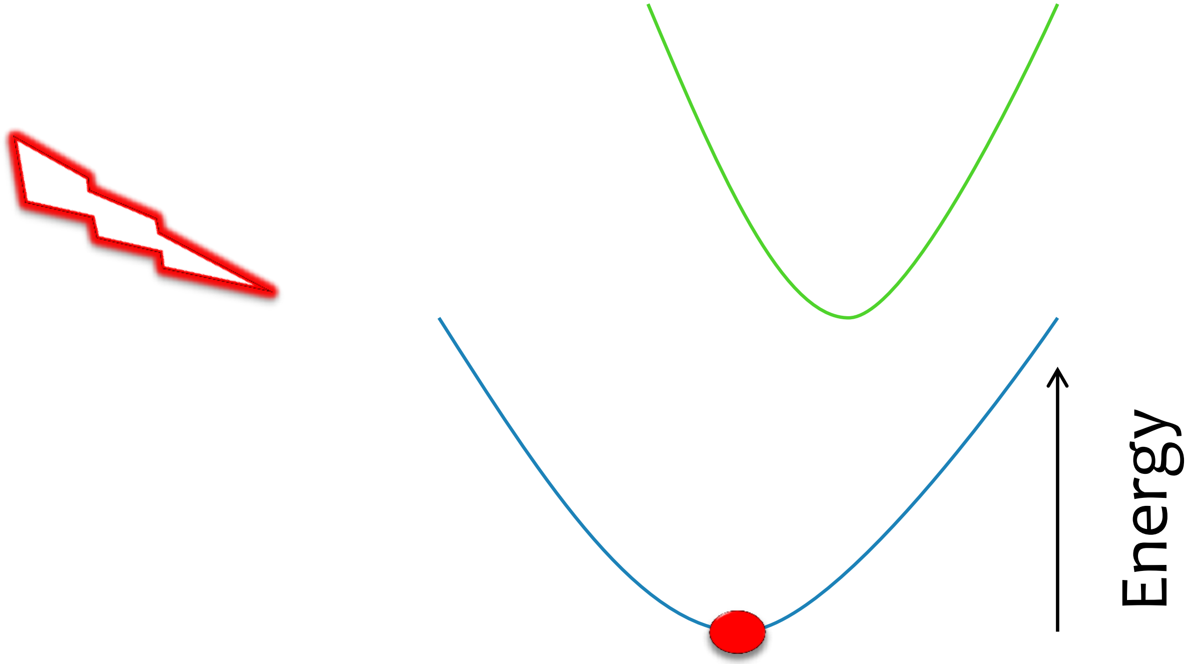
Electronic components

Solar energy conversion

How does light initiate device functions?

Light-harvesting

photons must first enter the material



Single molecules exhibit quantized electronic energy levels

An incoming photon can be absorbed causing an electron to jump to a higher energy state...

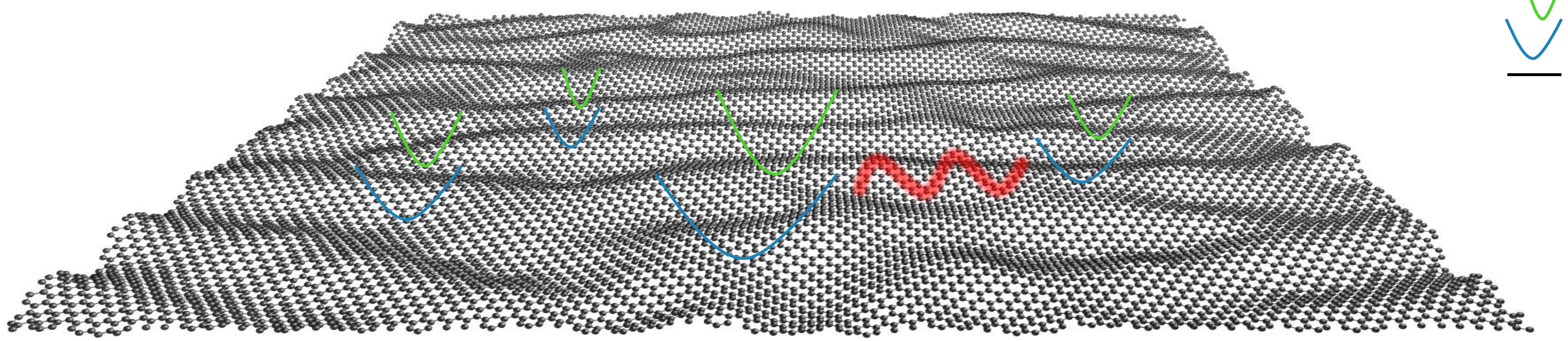
The system then begins to evolve on a new potential energy surface – giving rise to unique quantum mechanical behavior.

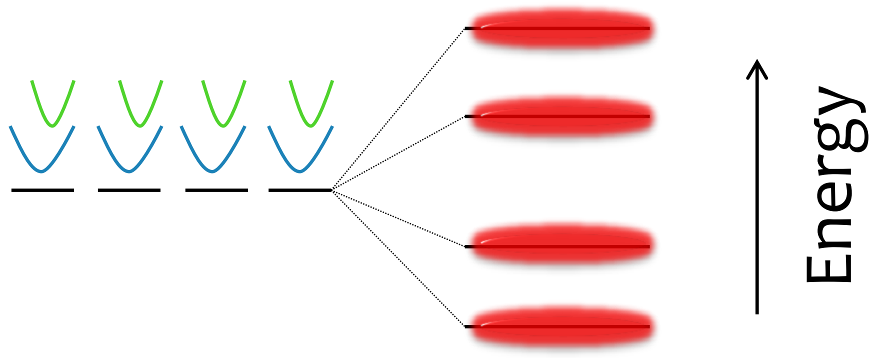
Creating an "**exciton**" (electron-hole pair)

How does light initiate device functions?

Excitation energy transfer

photon energy is propagated through the material via the electronic and nuclear wavefunctions

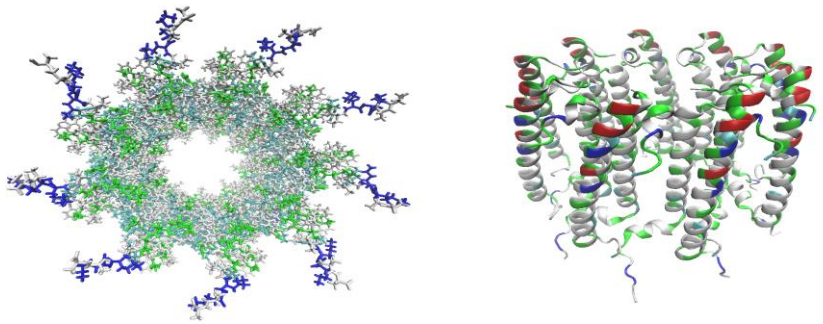




Design of photonic devices

Can *natural* photosynthetic systems provide revolutionary design principles?

- Strong light absorption
- High energy transfer efficiency

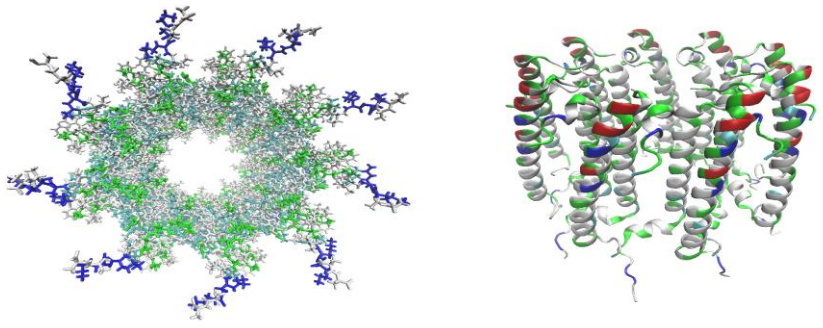


Light-harvesting complex II (LH2)

Design of photonic devices

Can *natural* photosynthetic systems provide revolutionary design principles?

- Functionality not fully understood
- Fabrication of large complexes extremely difficult



Light-harvesting complex II (LH2)

Empirical exciton framework

Exciton Hamiltonian

Individual fragments

Predict emergent properties and phenomena based on ...

sma...

ma...

functional theory (DFT)

$$H = \begin{bmatrix} E_0 & V_{0,1}^{0,1} & V_{0,1}^{0,2} & \cdots & V_{0,N}^{0,2} \\ (V_{0,1}^{0,1})^* & E_1^1 & 0 & \cdots & V_{1,N}^{1,2} \\ (V_{0,1}^{0,2})^* & 0 & E_1^2 & \cdots & V_{1,N}^{2,2} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ (V_{0,N}^{0,2})^* & (V_{1,N}^{1,2})^* & (V_{1,N}^{2,2})^* & \cdots & E_N^k \end{bmatrix}$$

Cal...

ele...

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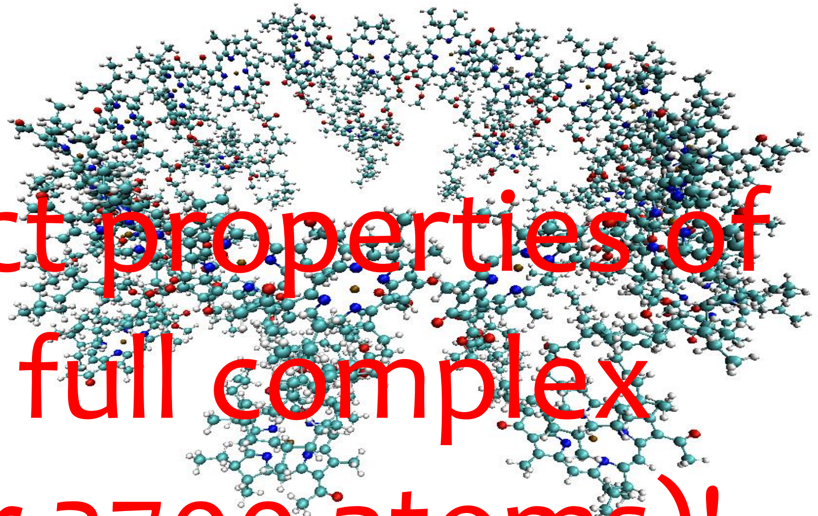
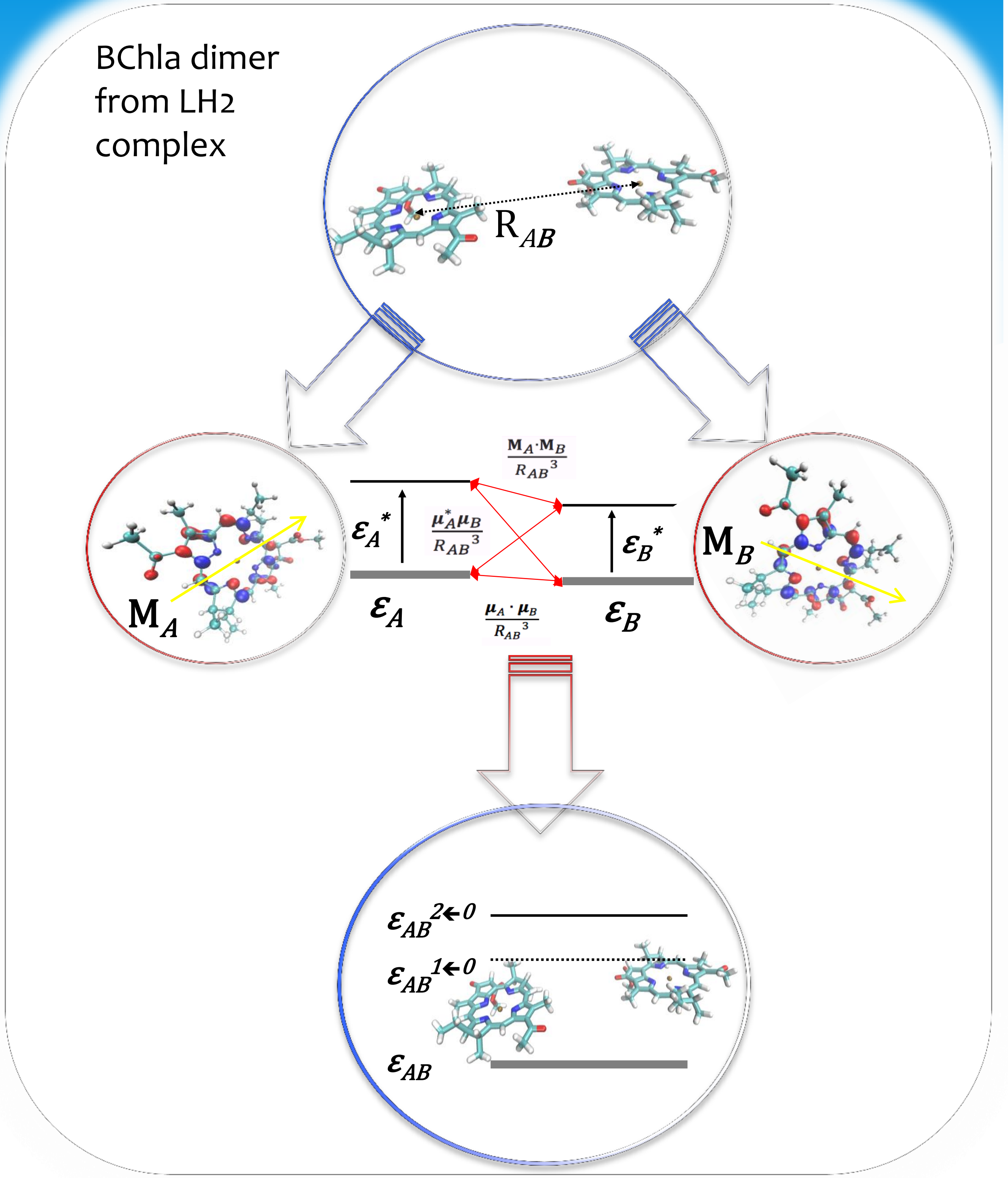
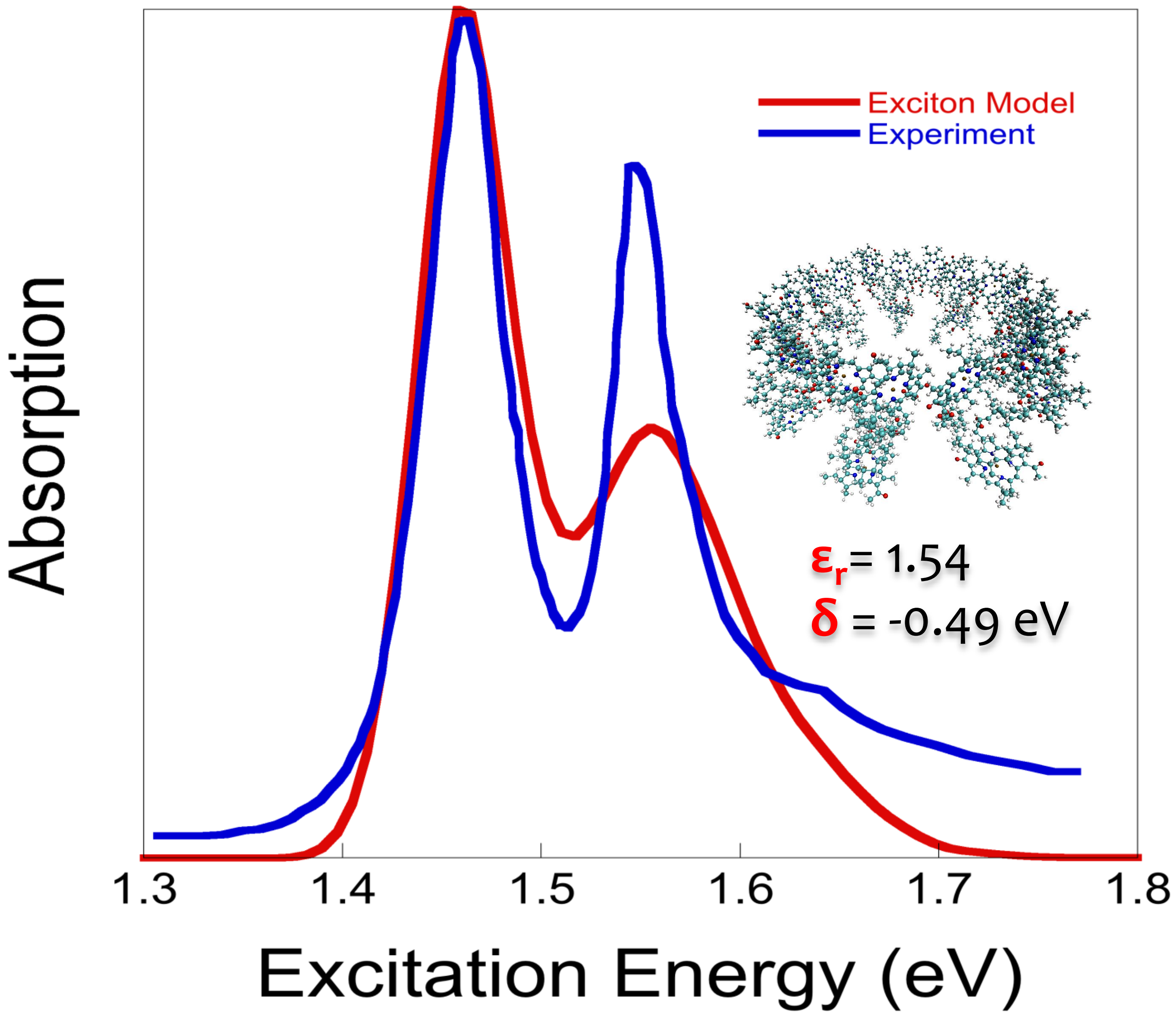
fur...



Predict properties of the full complex (over 3700 atoms)!



Exciton model generation



Optimize model based on empirical training data

Linear absorption spectrum of *Rhodobacter sphaeroids* at 300K

(E. Harel, et al., PNAS 2012)

$$V_{i,j}^{k\leftarrow 0,\ell\leftarrow 0} = \frac{1}{\varepsilon_r}\frac{\boldsymbol{M}_i^{k\leftarrow 0}\cdot \boldsymbol{M}_j^{\ell\leftarrow 0} - 3(\boldsymbol{n}_{ij}\cdot \boldsymbol{M}_i^{k\leftarrow 0})(\boldsymbol{n}_{ij}\cdot \boldsymbol{M}_j^{\ell\leftarrow 0})}{R_{ij}^3}$$

$$E_i^k = \sum_{j\neq i} \varepsilon_j + \varepsilon_i^k + \delta$$

Exciton dynamics

Atomic structure and *electronic coupling* direct the flow of excitation energy

Electronic structure causes ***nuclear*** reorganization

Nuclear motion induces ***electronic*** transitions

Simultaneous propagation of nuclear and electronic wavefunctions

At each timestep:

- Calculate excitonic states
- Compute nuclear forces

$$\boldsymbol{F}_I = -\langle \psi_I | \frac{\partial H_{ex}}{\partial \boldsymbol{R}} | \psi_I \rangle$$

and non-adiabatic couplings

$$\boldsymbol{d}_{IJ} = \frac{\langle \psi_I | \frac{\partial H_{ex}}{\partial \boldsymbol{R}} | \psi_J \rangle}{\varepsilon_J - \varepsilon_I}$$

- Propagate by *dt*

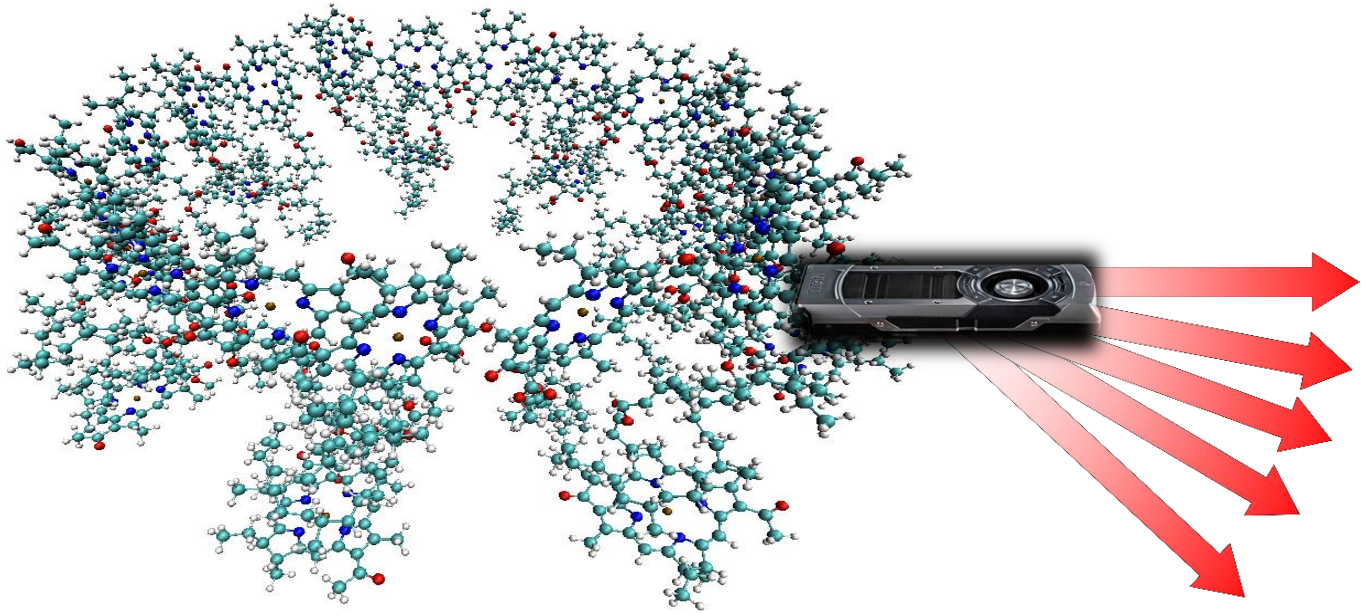
$$i \frac{\partial}{\partial t} \Psi(\boldsymbol{r}, \boldsymbol{R}, t) = \hat{H} \Psi(\boldsymbol{r}, \boldsymbol{R}, t)$$

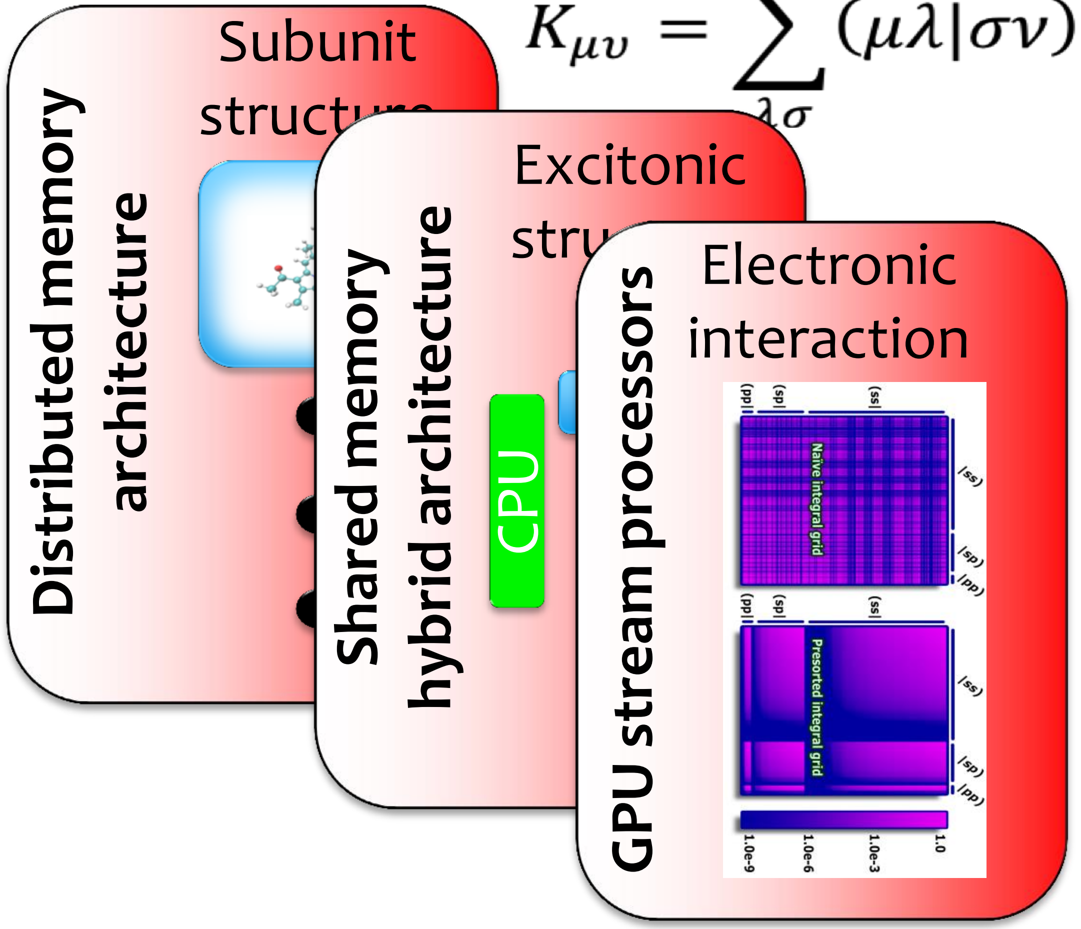
Massively parallel atomistic simulations

$$H = \begin{bmatrix} E_0 & V_{0,1}^{0,1} & V_{0,1}^{0,2} & \cdots & V_{0,N}^{0,2} \\ \left(V_{0,1}^{0,1}\right)^* & E_1^1 & 0 & & \\ \left(V_{0,1}^{0,2}\right)^* & 0 & E_1^2 & & \\ \vdots & \vdots & \vdots & & \\ \left(V_{0,N}^{0,2}\right)^* & \left(V_{1,N}^{1,2}\right)^* & \left(V_{1,N}^{2,2}\right)^* & & \end{bmatrix}$$

$$J_{\mu\nu} = \sum_{\lambda\sigma}^{N} (\mu\nu|\lambda\sigma)\, P_{\lambda\sigma}$$

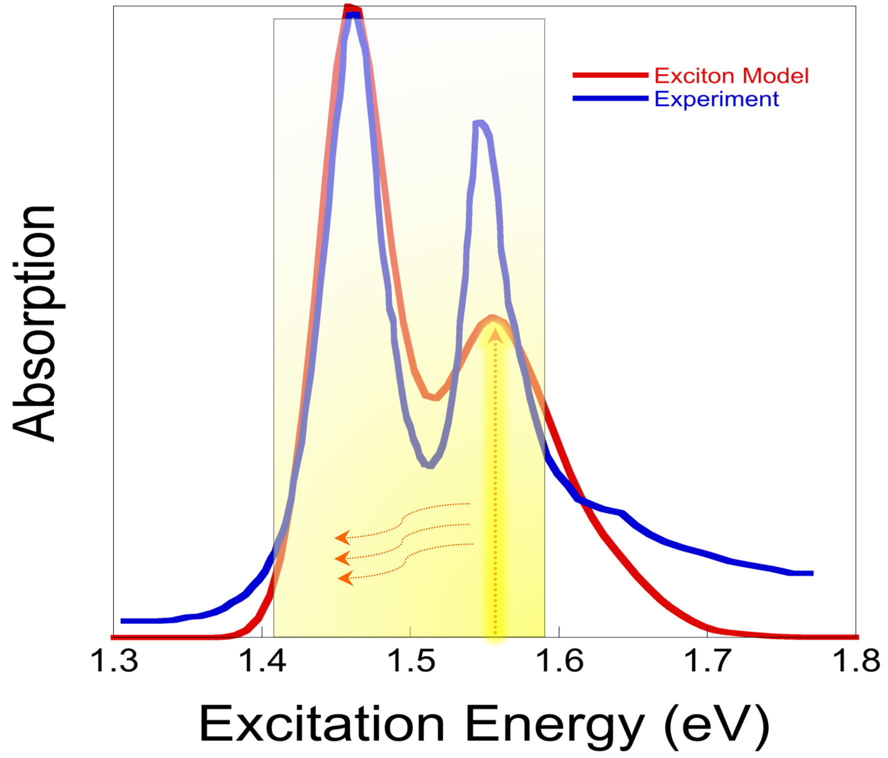
$$K_{\mu\nu} = \sum_{\lambda\sigma}^{N} (\mu\lambda|\sigma\nu)\, P_{\lambda\sigma}$$





Exciton dynamics

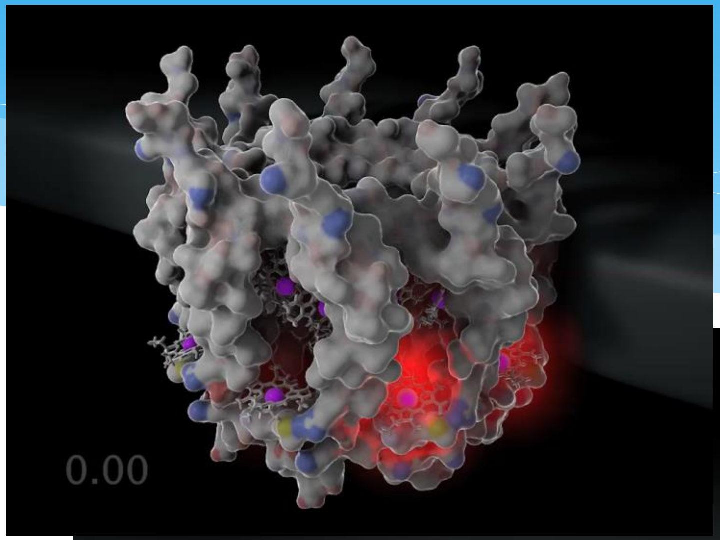
Simulation of electronic excitation and dynamics of LH2 Bchlas chromophores

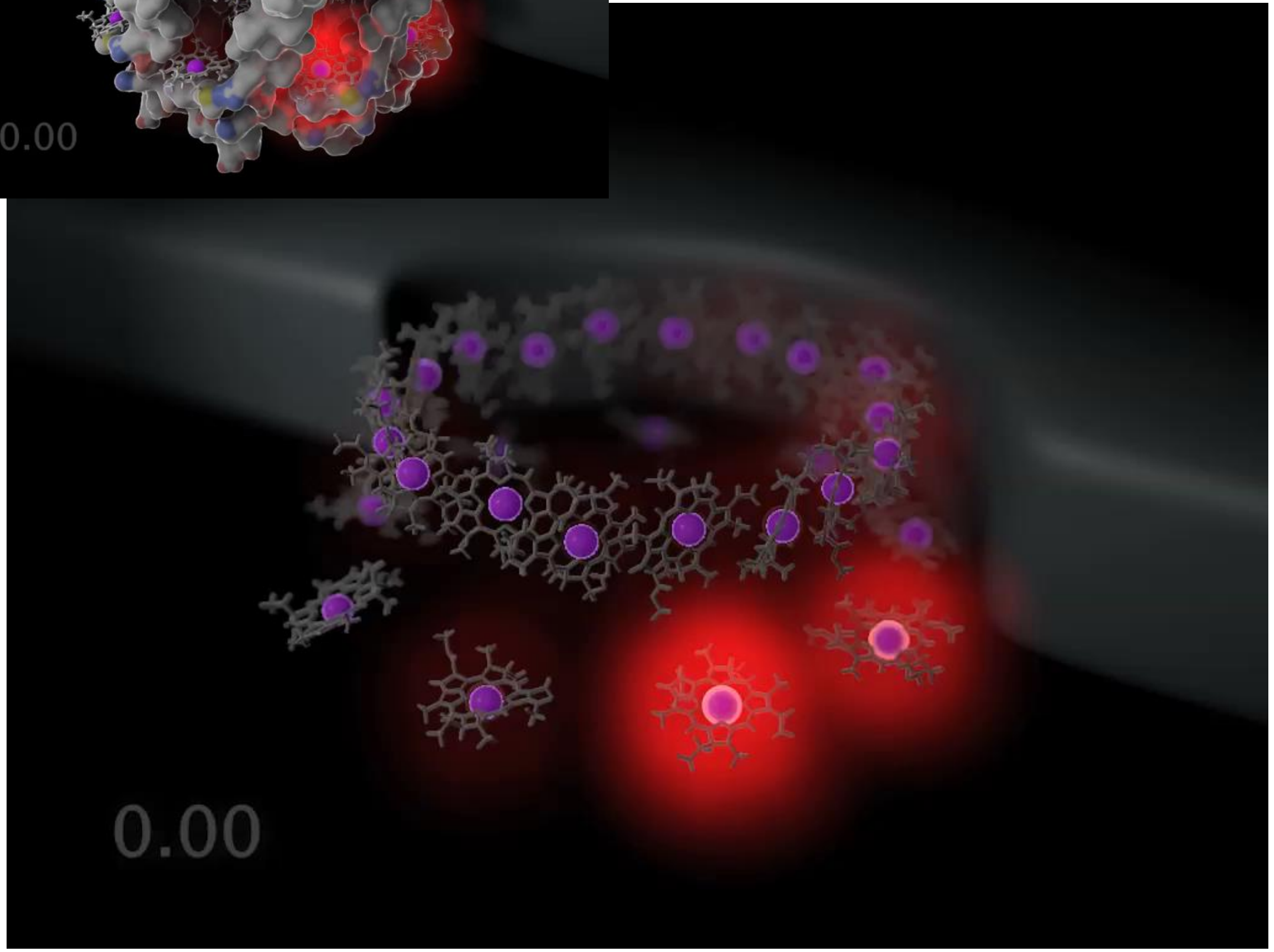


Excitation at t=0 fs

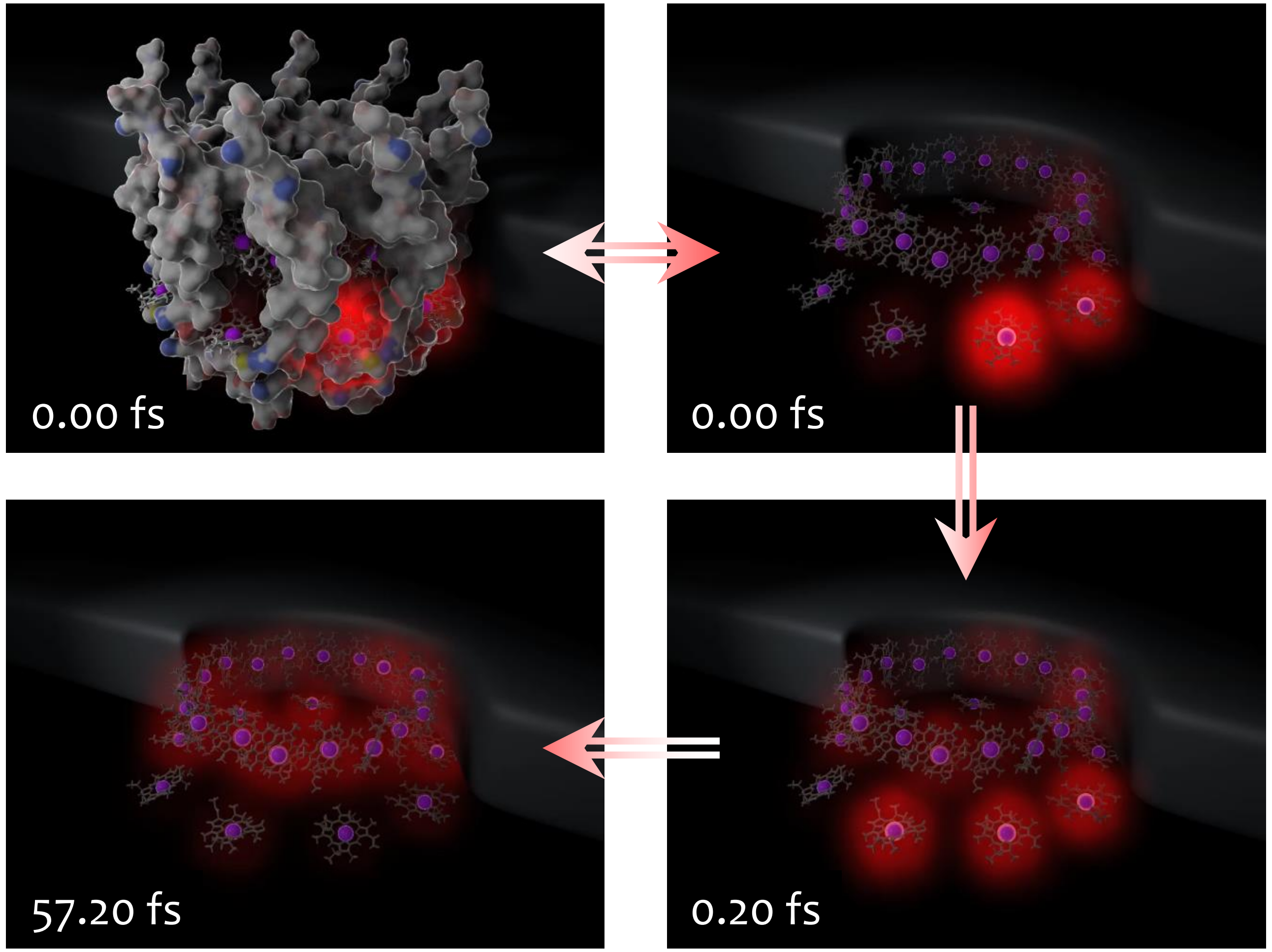
Exciton diffusion

Coherent fluctuations





Exciton dynamics



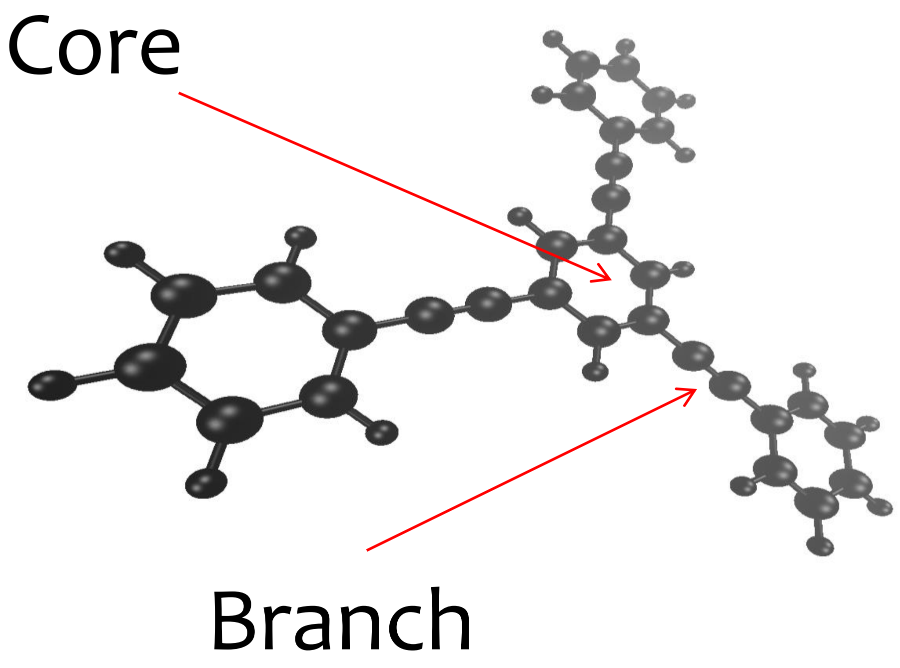
- *Spatial-energetic correlation*
- *Arrow of time: electronic entropy maximization*

Designing photosynthetic devices

Single molecules that absorb light at the periphery and transfer energy to the core

Phenylacetylene Dendrimers

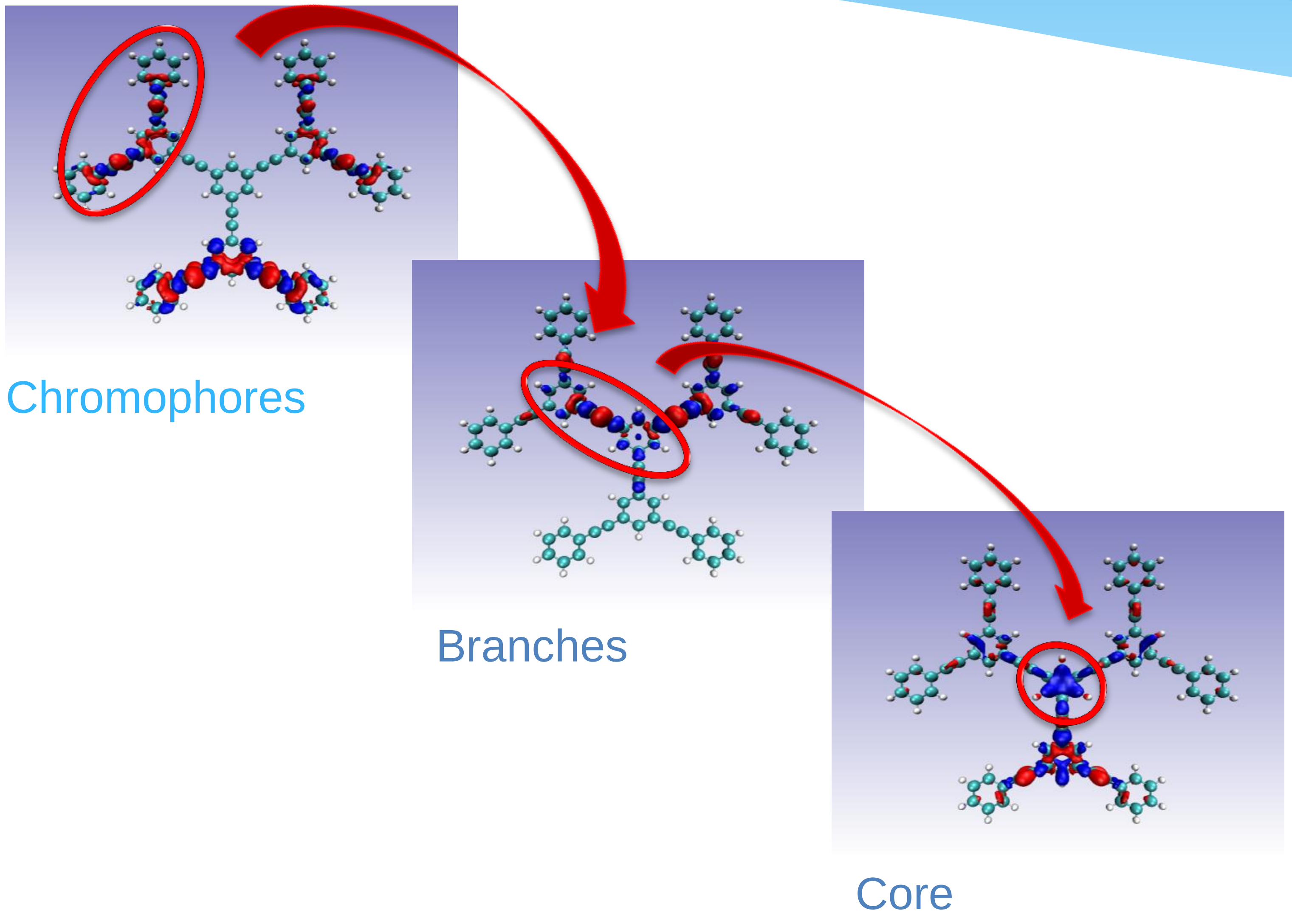
- *Branched, hierarchical structure*
- *Constructed from identical subunits*

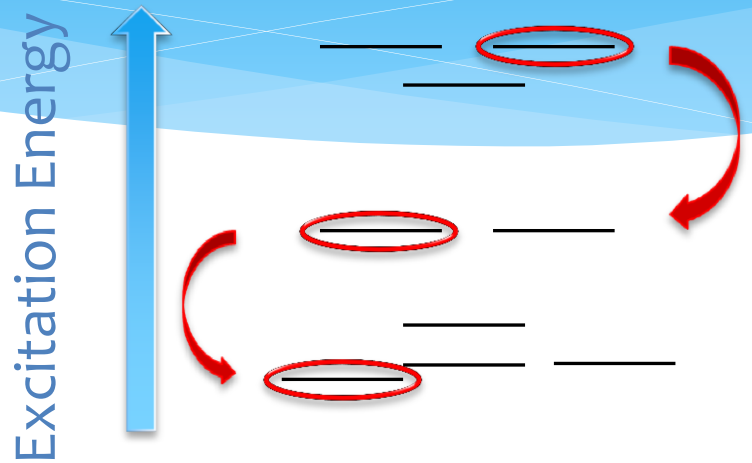


Design Objectives:

- *Controlled directional transport*
- *High quantum yield*

Intrinsic energy pathways



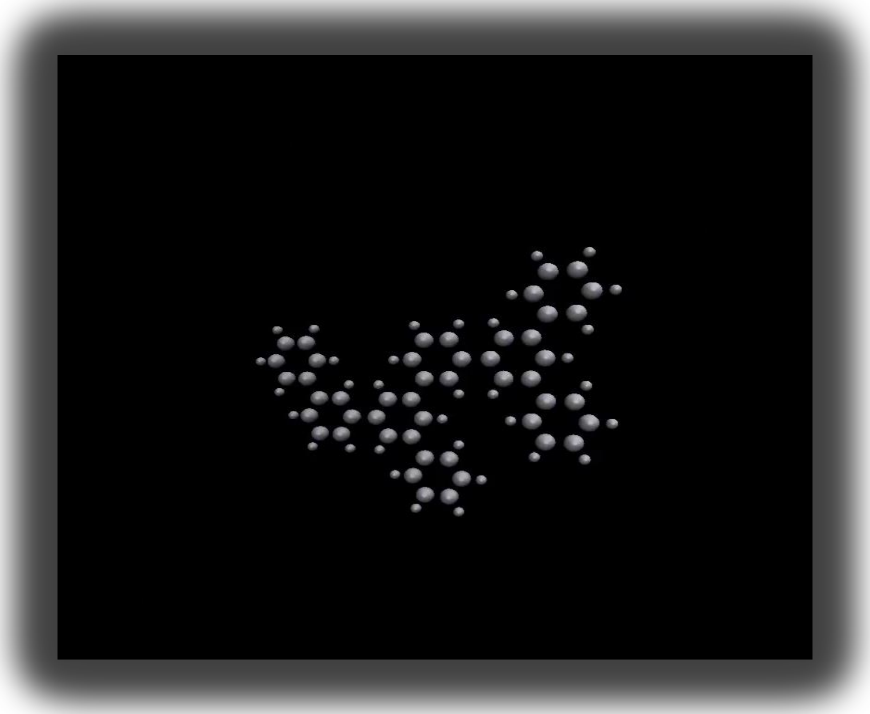


Spatial

Correlated transitions

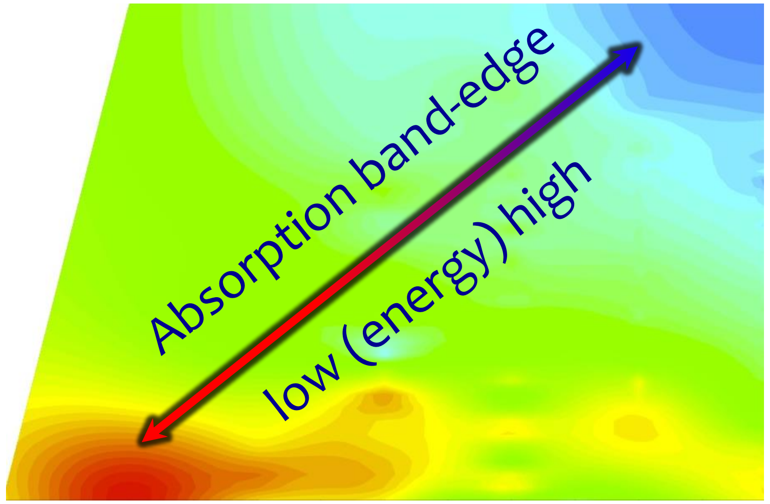
Energetic

Materials discovery



Structure generation:
Molecular combinatorics

Device performance prediction:
local kernel models



Molecular design space

Acknowledgements

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Questions?