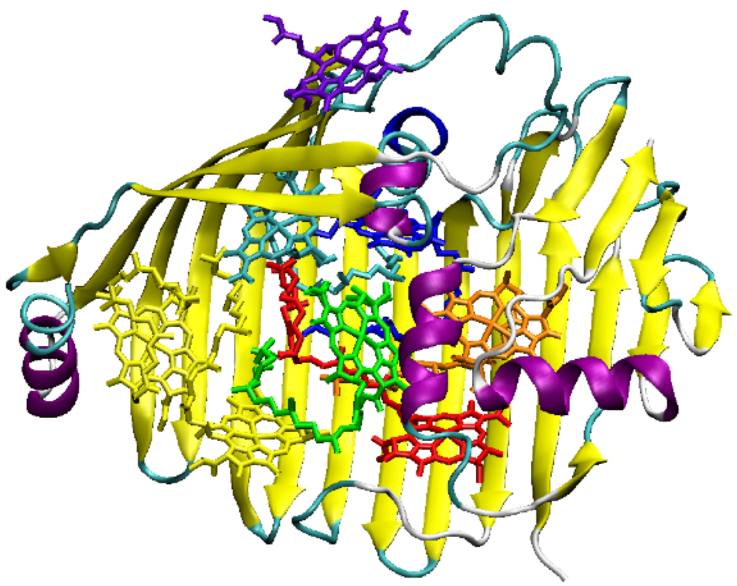
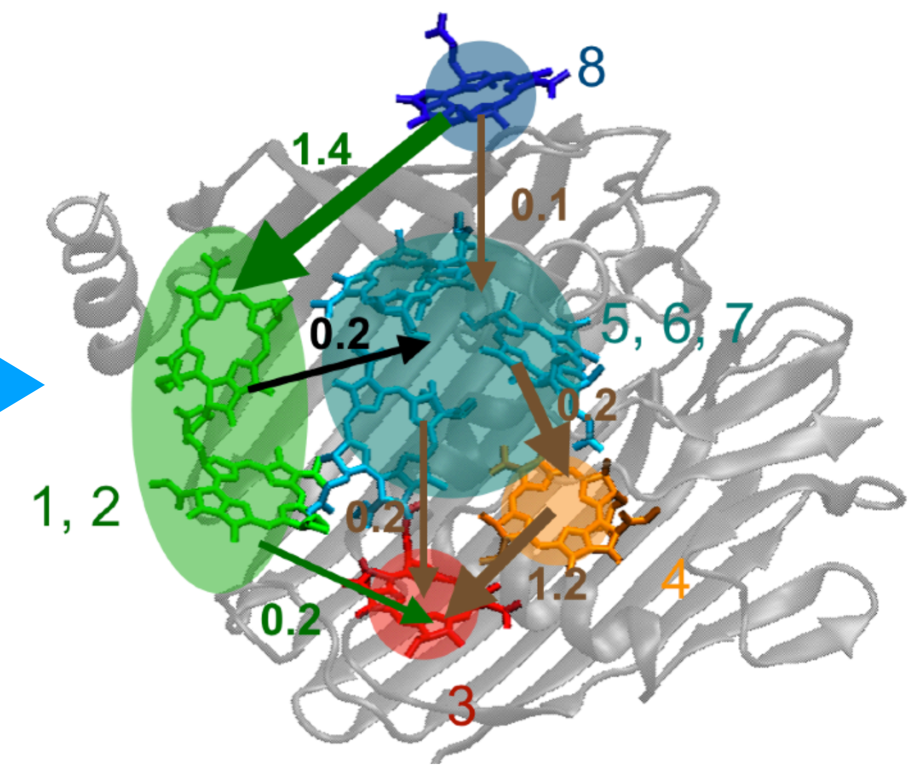
Towards a Systematic Coarse-Graining Method for Excitation Energy Transfer Networks: A Minimum-Cut Approach

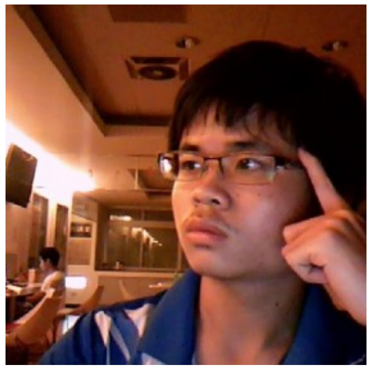


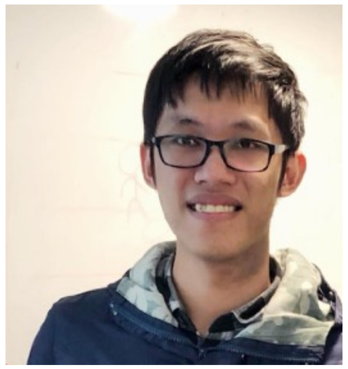
Coarse-Graining

Minimum-Cut Approach



Wei-Hsiang Tseng





Speaker: De-Wei Ye

Advisor: Yuan-Chung Cheng

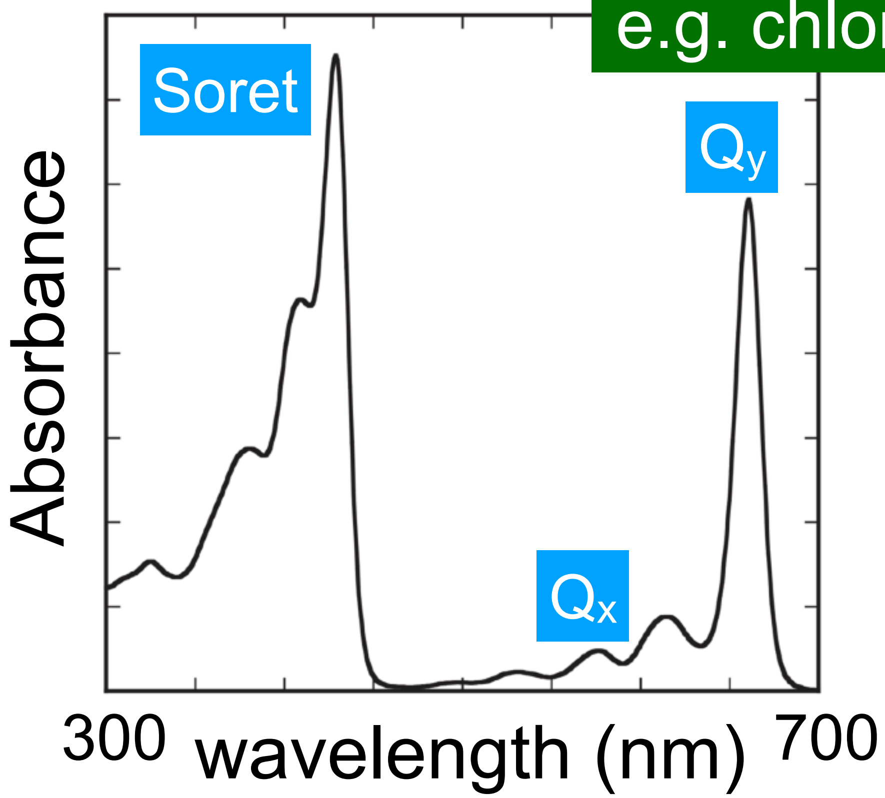
Thu 08 Feb 2018

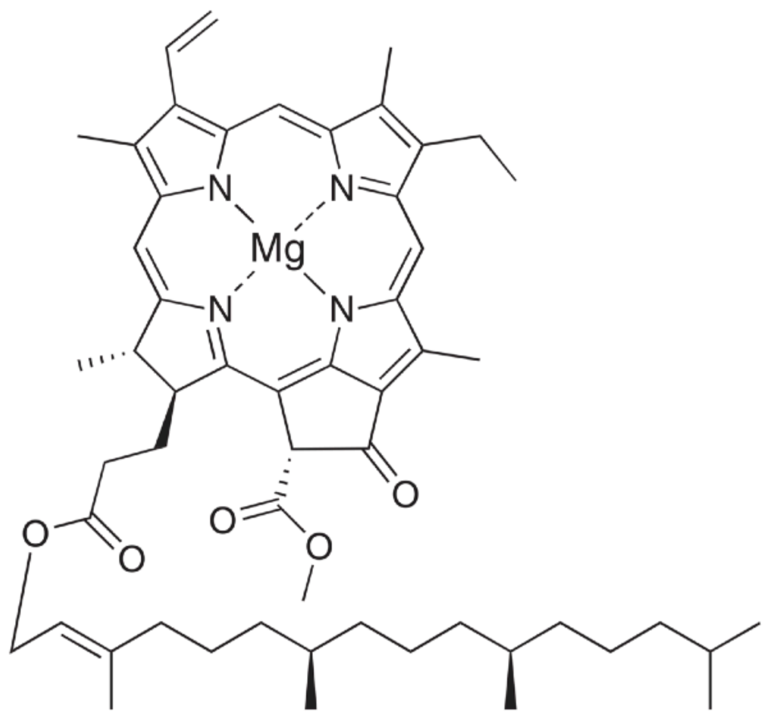
Outline

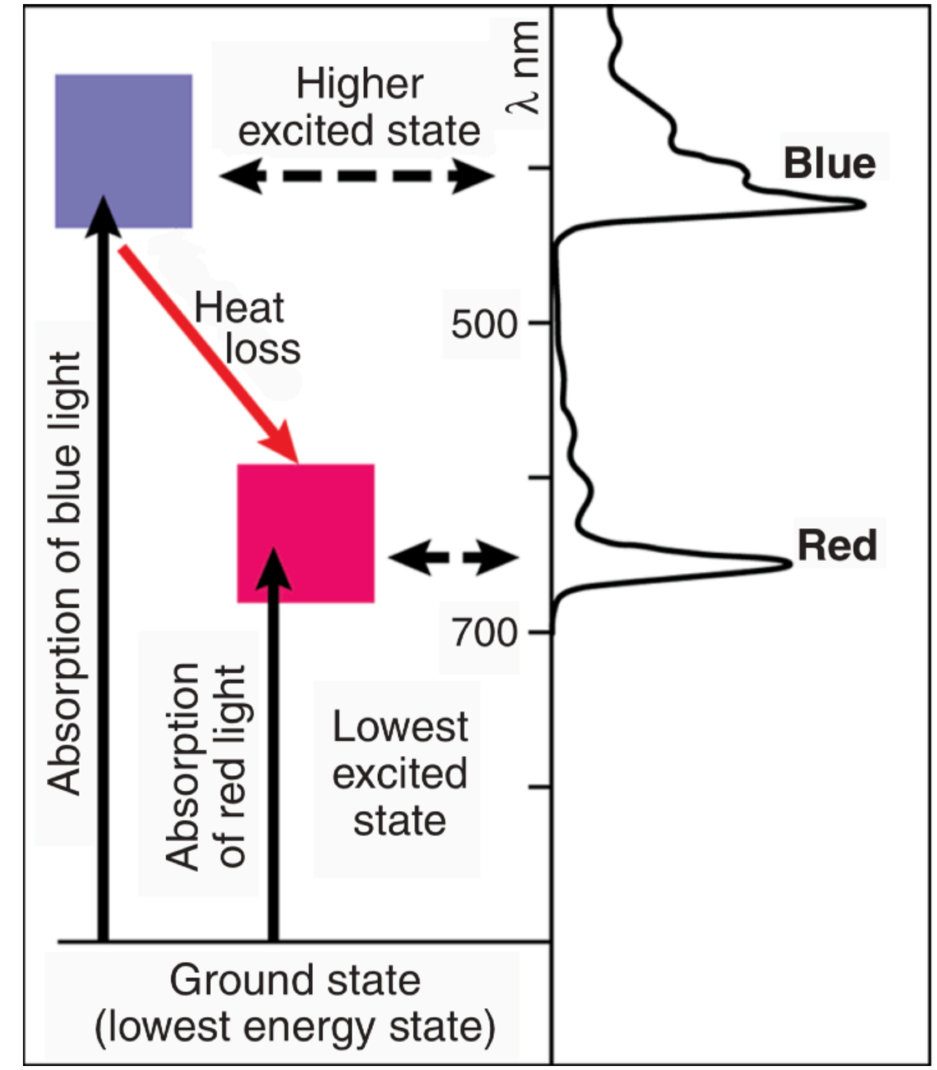
- **Theoretical backgrounds:**
  - Excitation energy transfer (EET) networks
  - The minimum-cut problem
- Methods:
  - A directed minimum-cut tree
  - Clustering methods
  - EET pathway analysis
- Results:
  - The FMO complex
  - The LHCII monomer

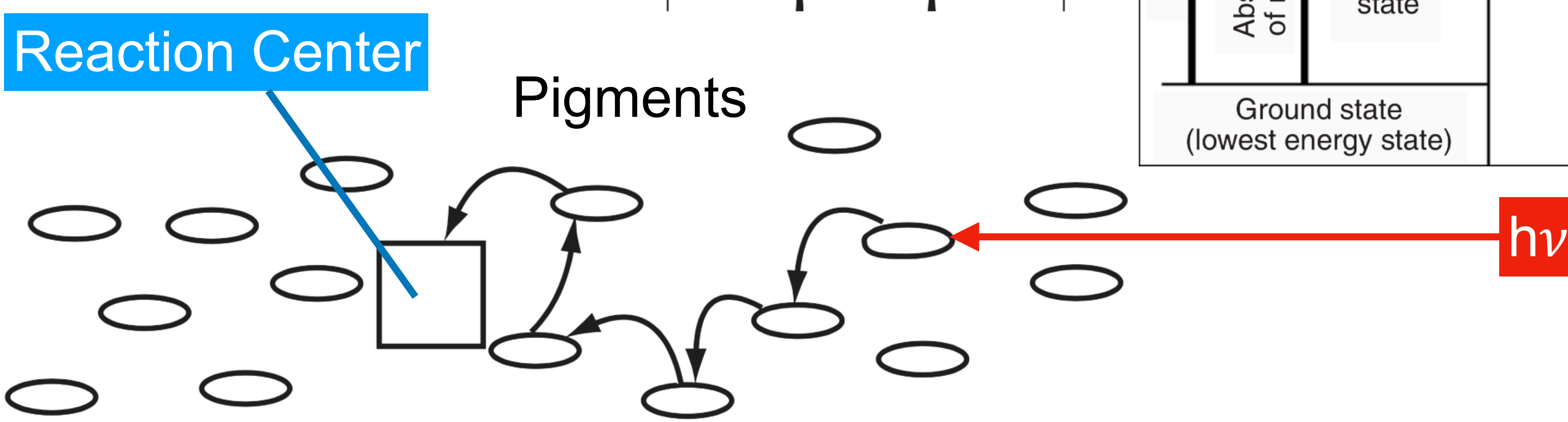
Light Harvesting

e.g. chlorophyll *a*









Excitation Energy Transfer (EET)

Blankenship, R. E. et al. *Science* **2011**, *332*, 805

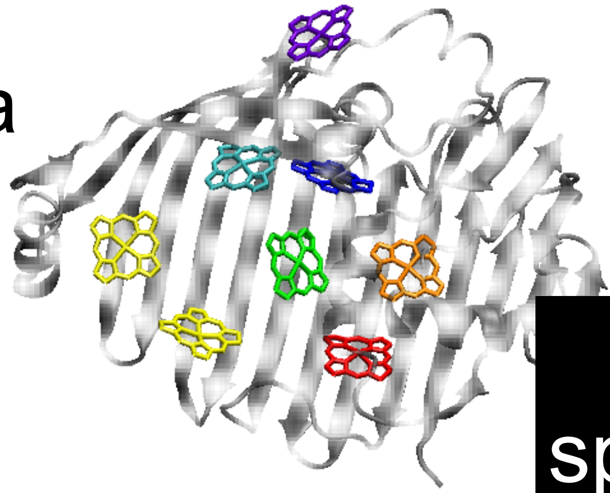
Blankenship, R. E. *Molecular Mechanisms of Photosynthesis* 2/e, Oxford, UK, **2014**

Obtaining the Effective Rate Matrix

Structure Data

↓

Chlorophylls (Sites)



Effective Hamiltonian

Basis transform

Parameters of spectral densities

Effective Rate matrix

$\mathbf{R}$

Frenkel exciton Hamiltonian

Modified Redfield theory

$$H = H_e + H_{ph} + H_{e-ph}$$

$$H_e = \sum_i \varepsilon_i |i\rangle\langle i|$$

$$H_{e-ph} = \sum_{i,j} |i\rangle\langle j| \cdot (H_{e-ph})_{ij}$$

$$H_{ph} = \sum_v \omega_v b_v^\dagger b_v$$

Population Transfer Dynamics

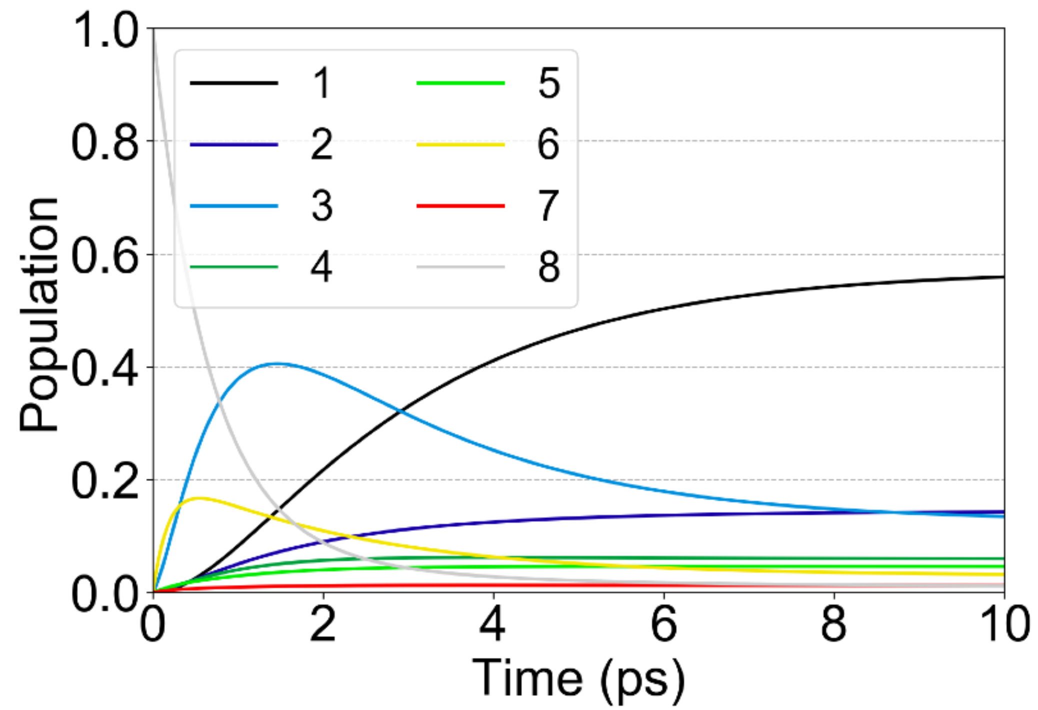
Effective Rate matrix

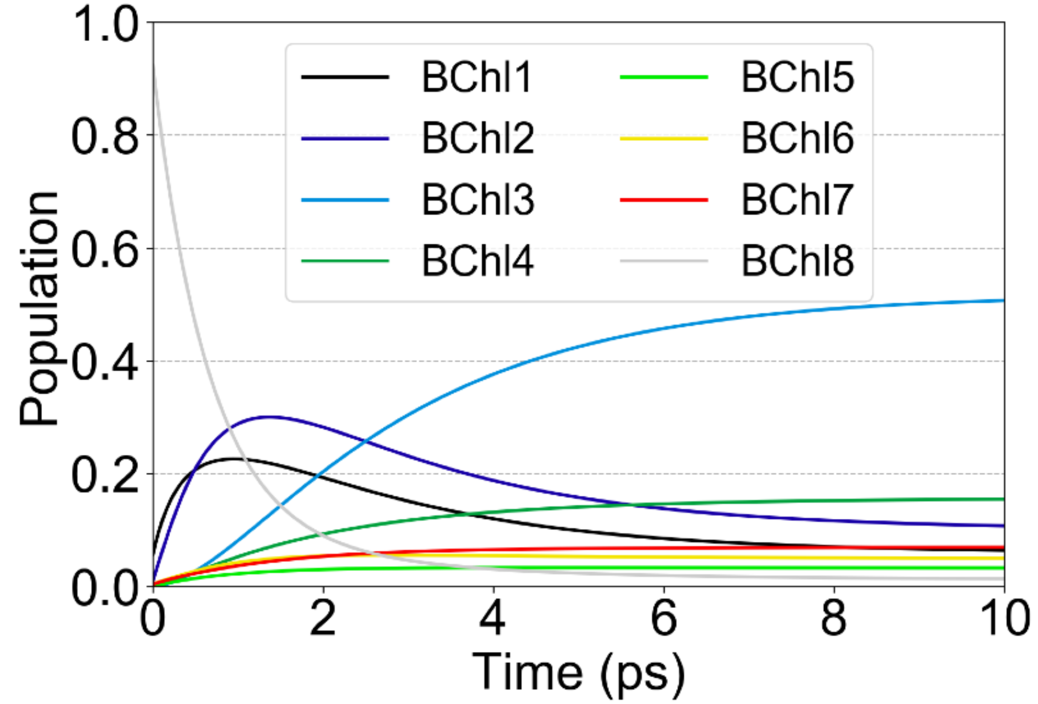
R

$$\frac{d}{dt}\mathrm{P}(t) = \mathbf{R}\mathrm{P}(t)$$

Coarse graining help us elucidate the complex EET network.

Dynamics

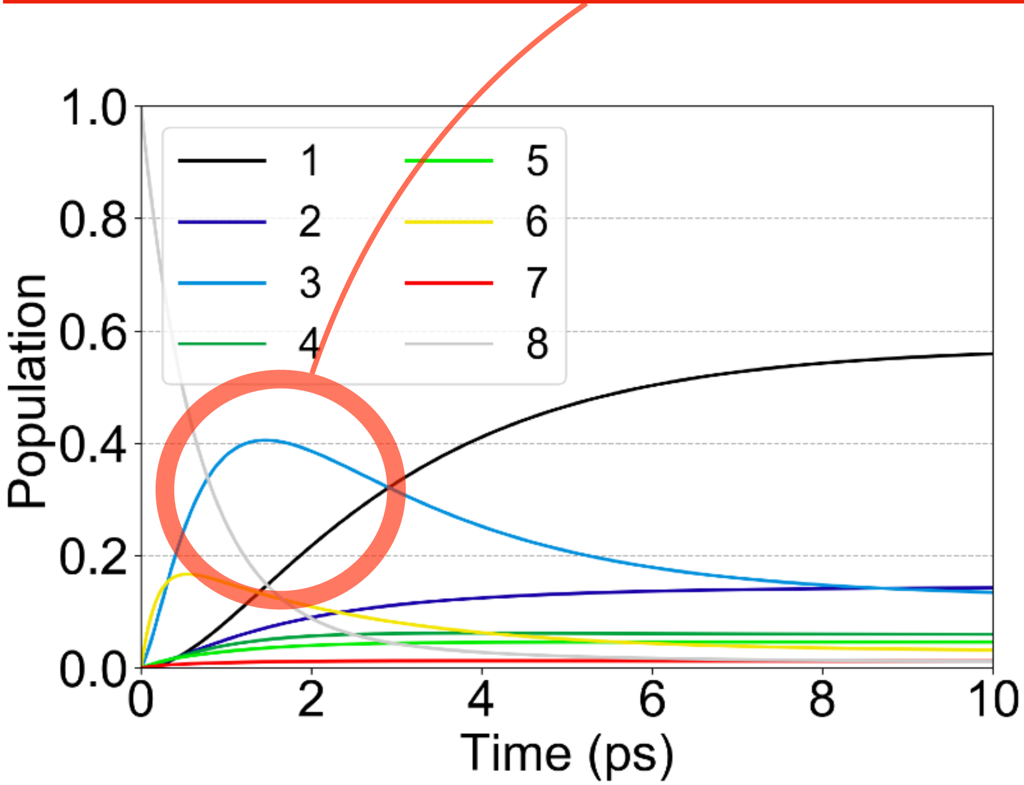




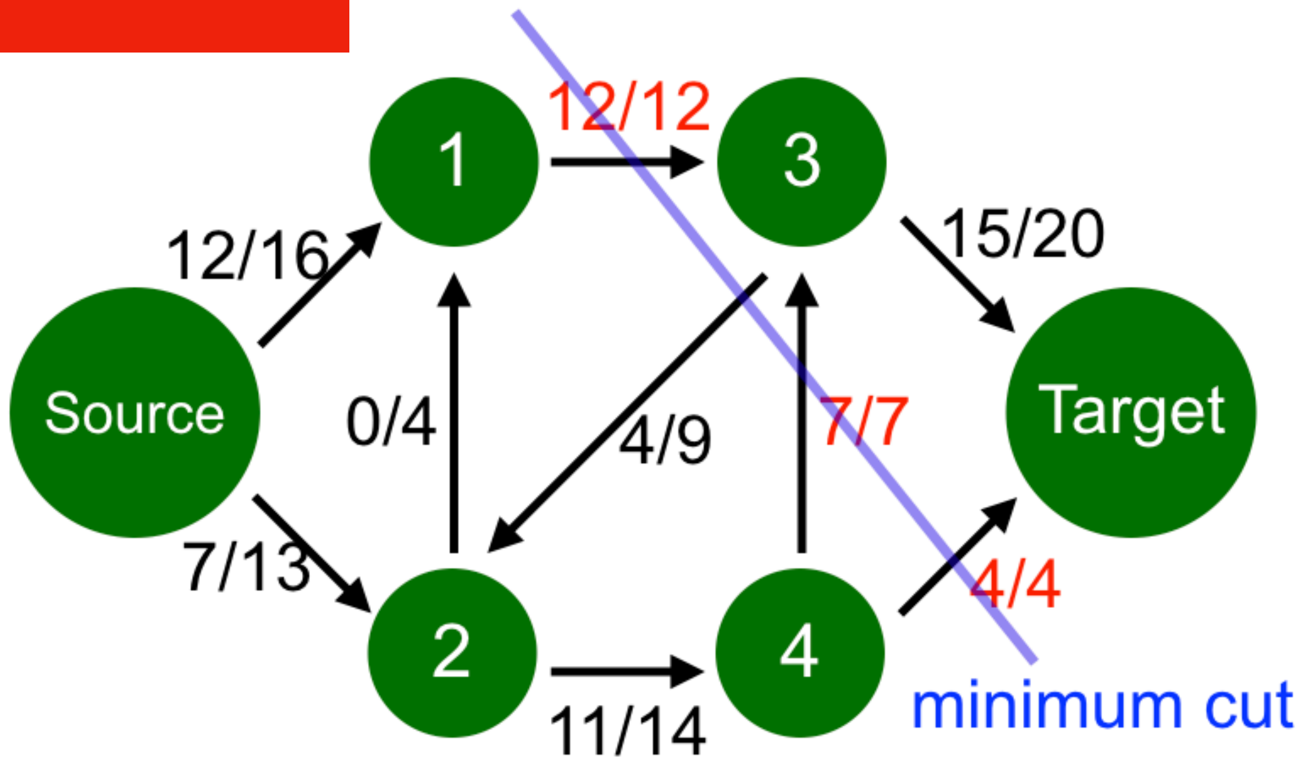
Minimum-Cut Maximum-Flow Theorem

- In a weighted graph, the total weights (capacities) of the edges in the minimum cut are proved to be equal to the maximum flow from a specific source node to another specific target node.

A long-lived state plays an important role in population transfer!



A weighted directed graph!



Ford, L. R.; Fulkerson, D. R. *Can. J. Math.* **1956**, *8*, 399

To Buildup a EET Network Model

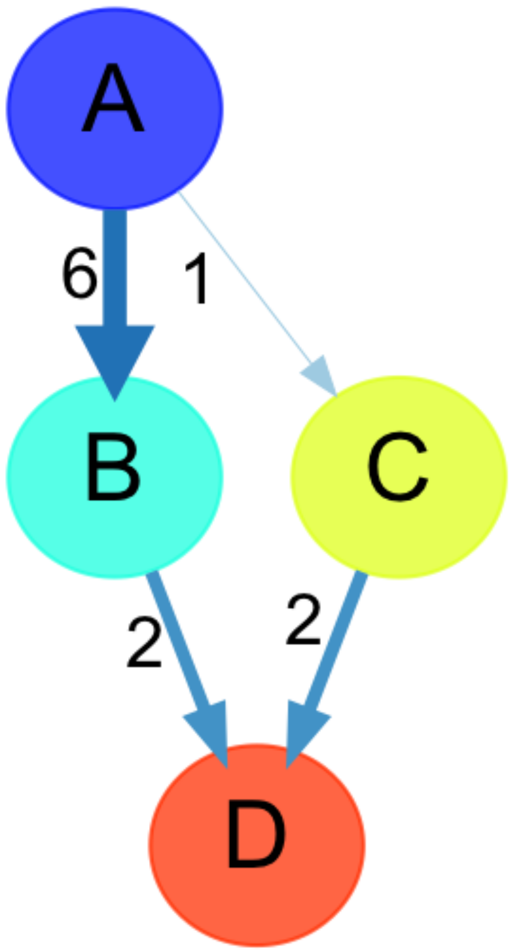
Effective Rate matrix

A weighted directed graph!

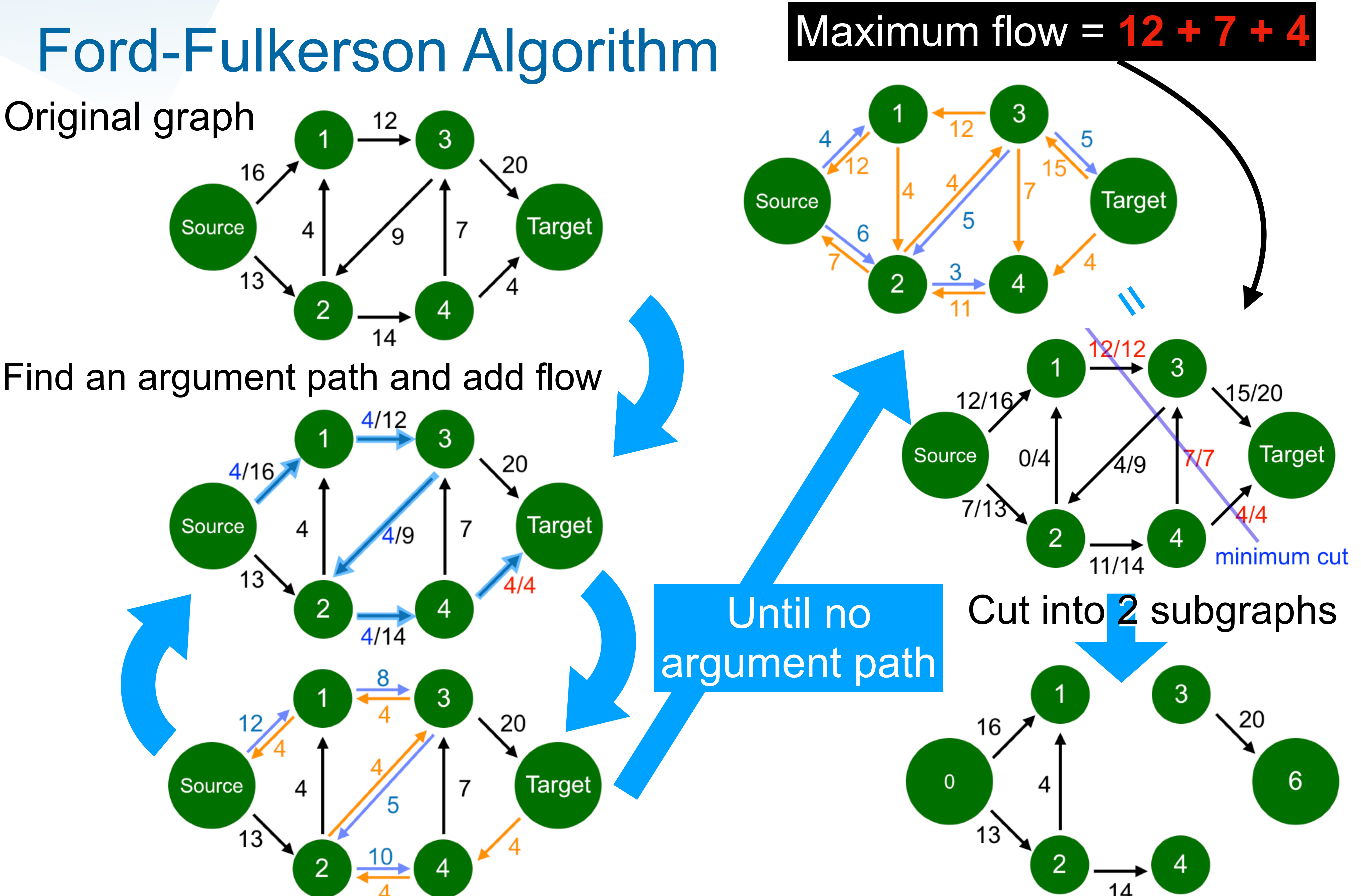
$\mathbf{R}$ $\quad R_{ji}$: rate from state i to state j

- Node i: exciton state i
- The capacity $c(i, j)$ of an edge $E(i, j)$: R_{ji}
- e.g.

	A	B	C	D
A	-7.4	0.0	0.0	0.0
B	6.0	-1.6	0.0	0.0
C	1.4	0.0	0.0	0.0
D	0.0	1.6	2.0	0.0



Ford-Fulkerson Algorithm



Ford, L. R.; Fulkerson, D. R. *Can. J. Math.* **1956**, *8*, 399

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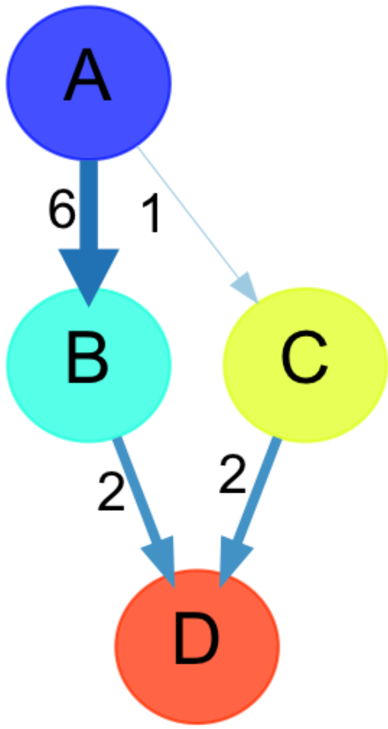
A Directed Minimum-Cut Tree



Tree Construction

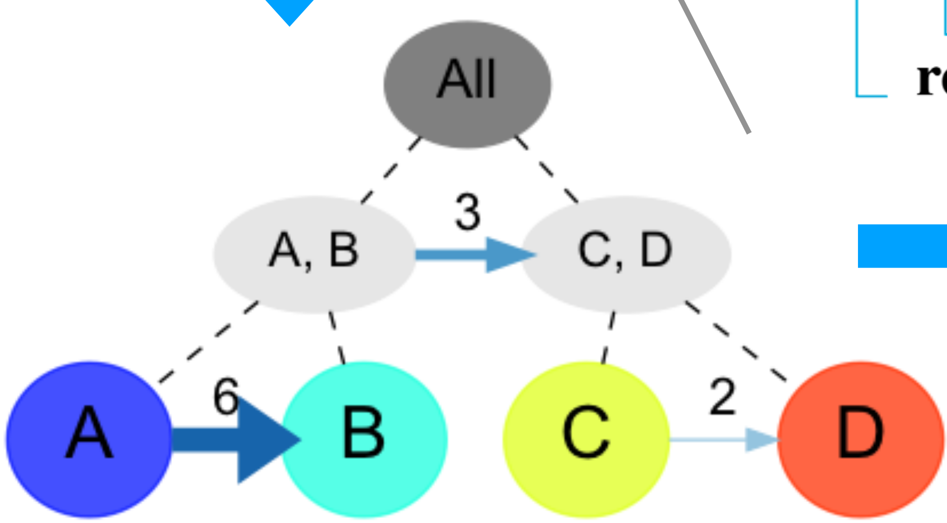
Algorithm 2: Construction of the Directed Minimum-Cut Tree

Input: an EET network G

Output: a directed minimum-cut tree T of G

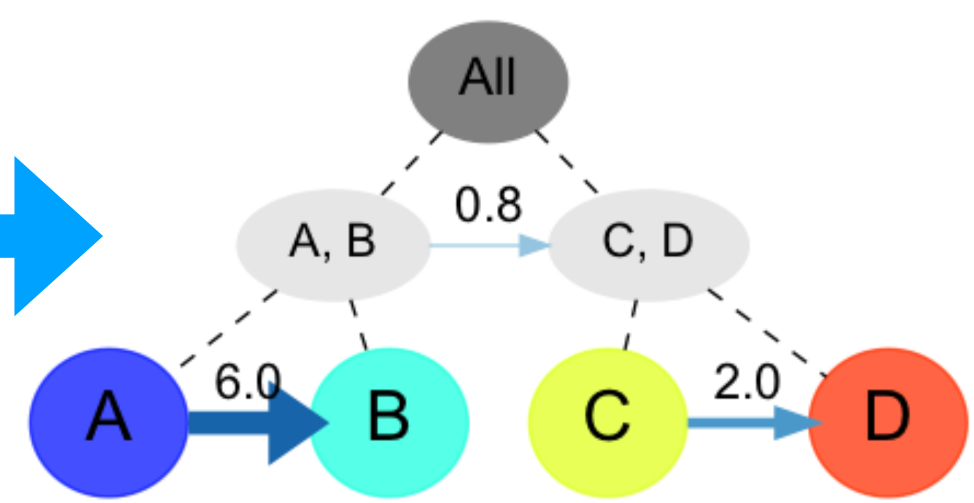
Function `Build`(G):

- T = an empty root `// Initialize` T
- T.top = G
- **if** $G.size > 1$ **then**
  - s = `argmax`(energies of states $\in G$)
  - t = `argmin`(energies of states $\in G$)
  - $T.maxflow, G_r$ = `FFA`(G, s, t)
  - `// use Breadth-First-Search(BFS) to determine the subgraph`
  - subgraph G_s = `BFS`(G_r, s)
  - subgraph $G_t = G - G_s$
  - $T.left\_root$ = `Build`(G_s)
  - $T.right\_root$ = `Build`(G_t)
- **return** T

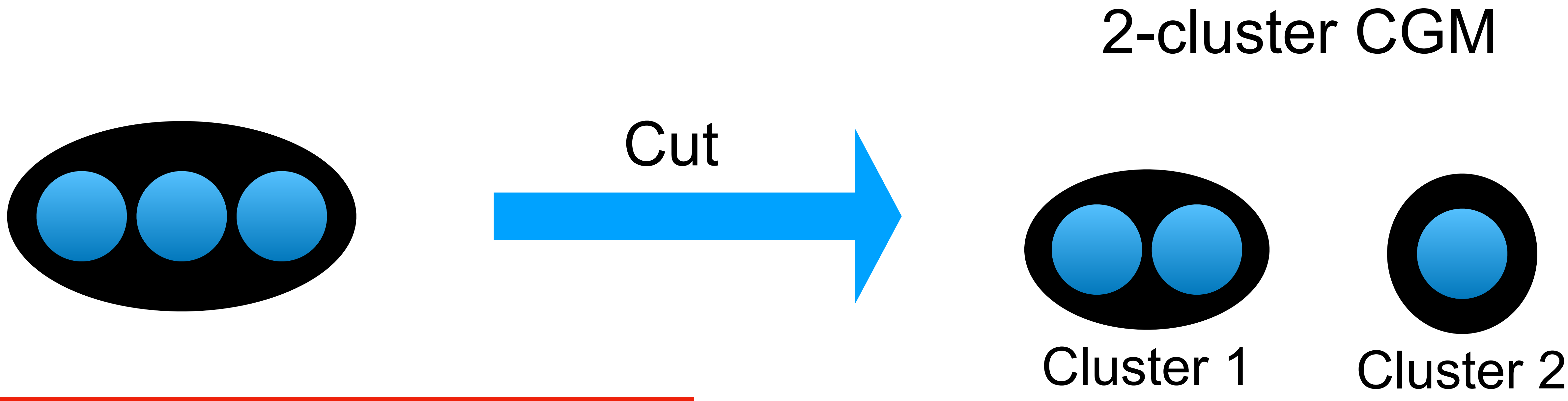


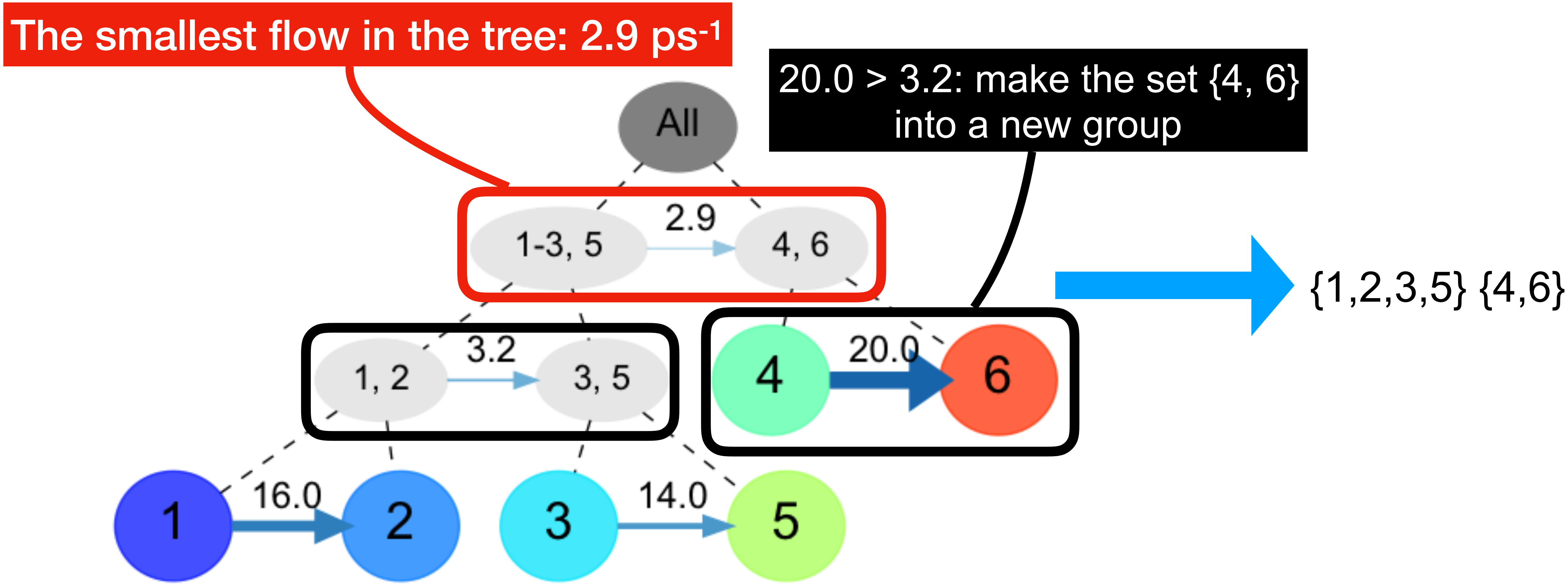
Normalized

$$f_{norm} = \frac{f}{N(S) \times N(T)}$$

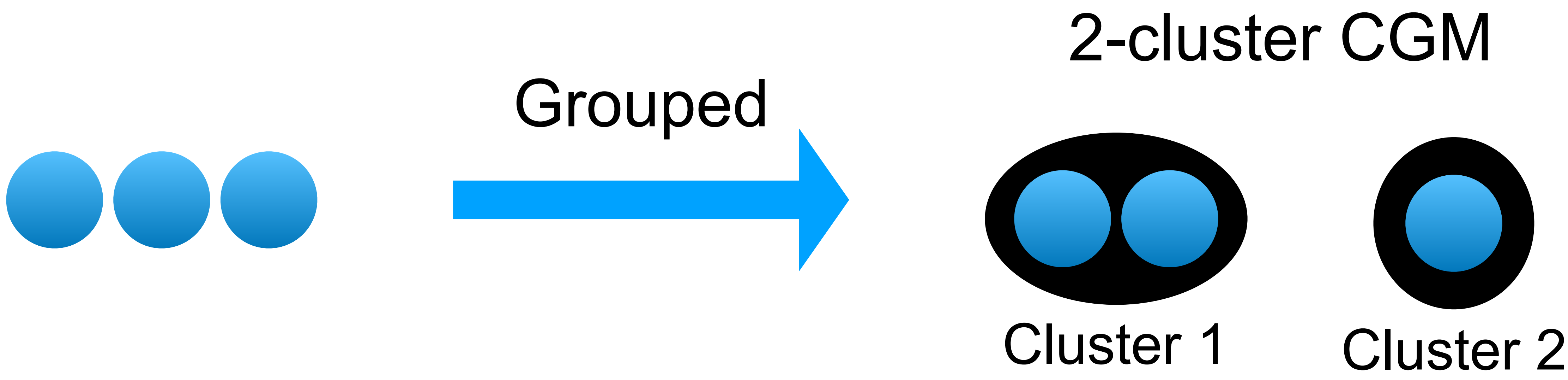


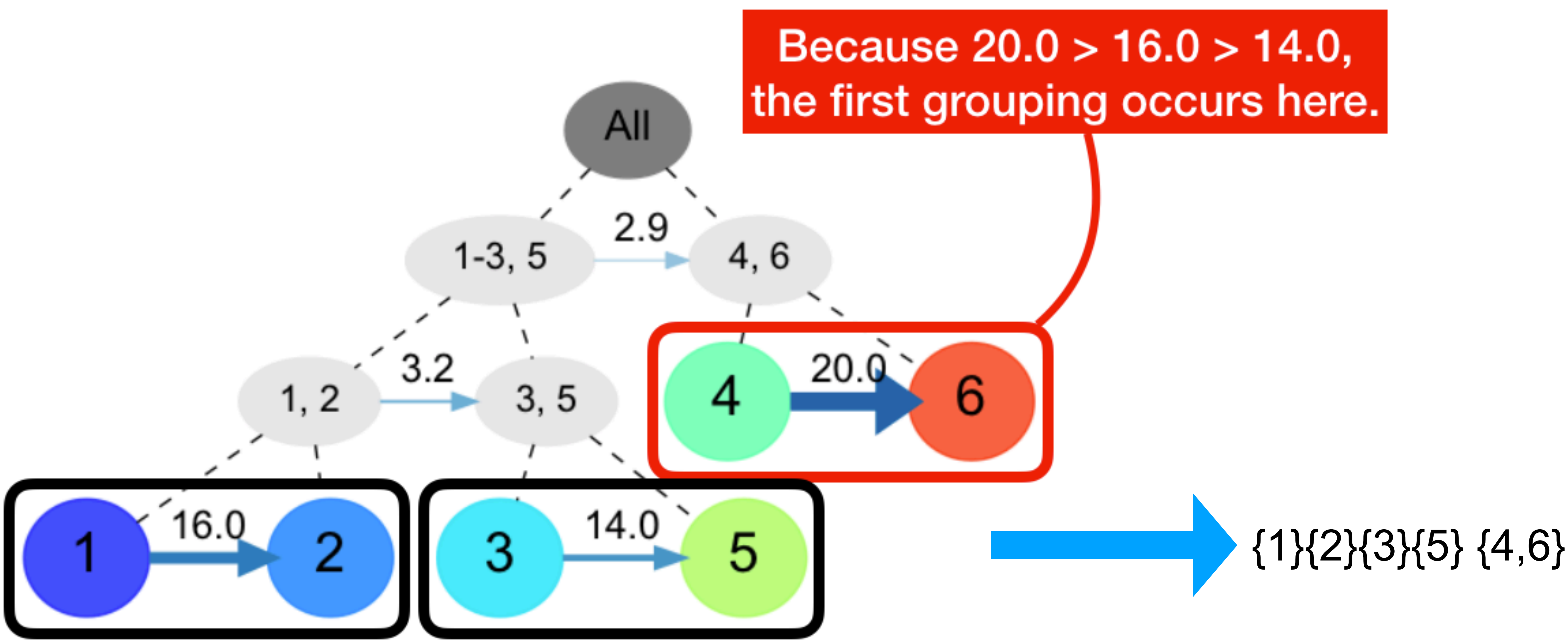
Top-Down Clustering (TDC) Method



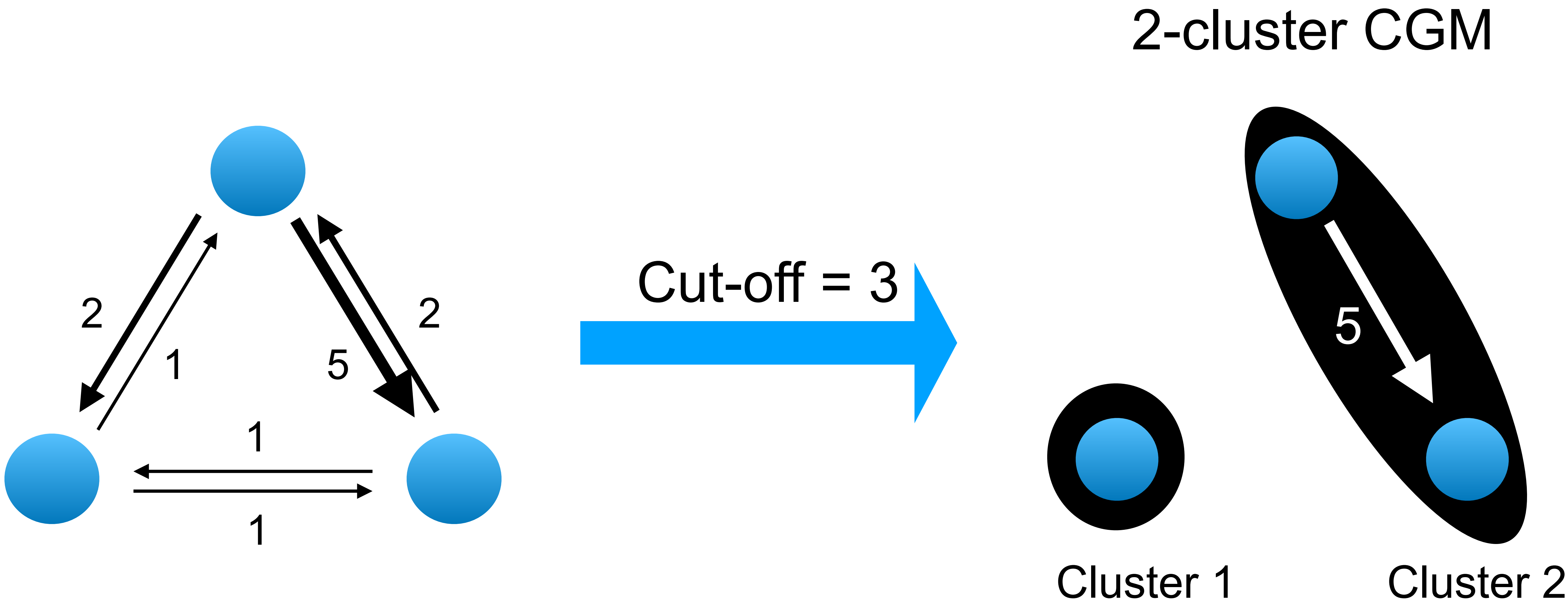


Bottom-Up Clustering (BUC) Method



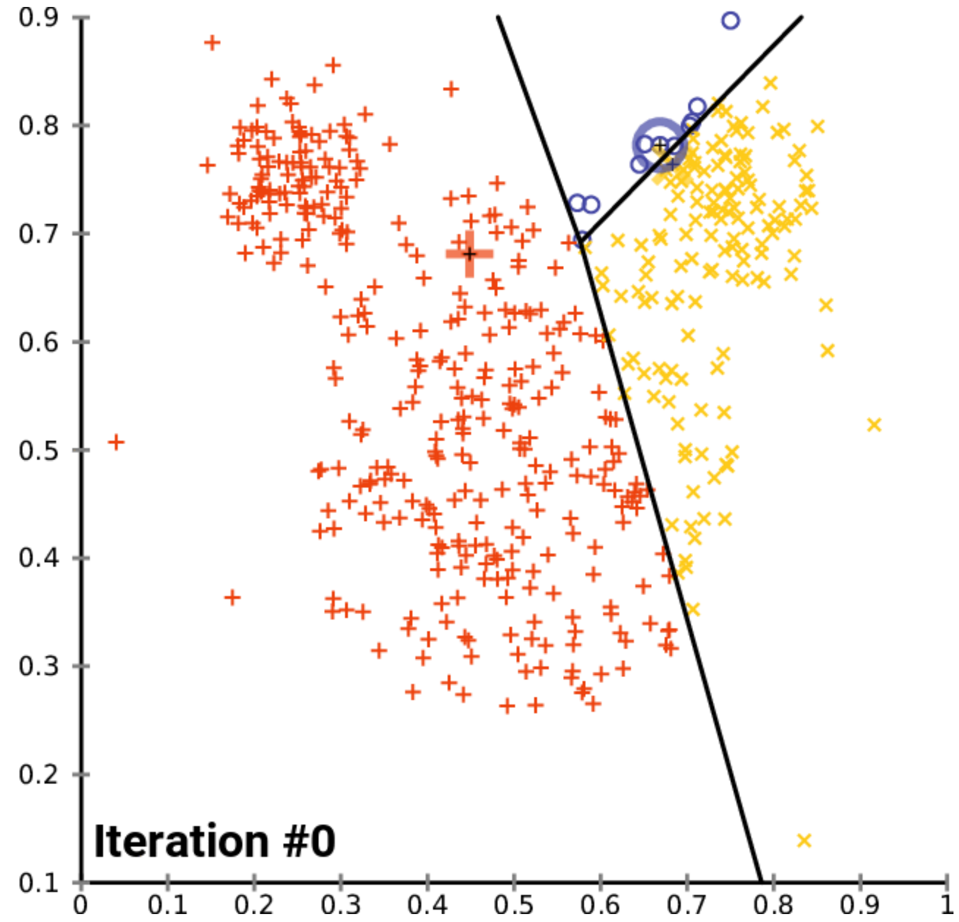


Directly Cut-off (DC) Method



K-Means-like (KM) Method

K-Means:



Chire, https://commons.wikimedia.org/w/index.php?curid=59409335

- K-Means-like method:
  - Minimize the variance in each cluster:

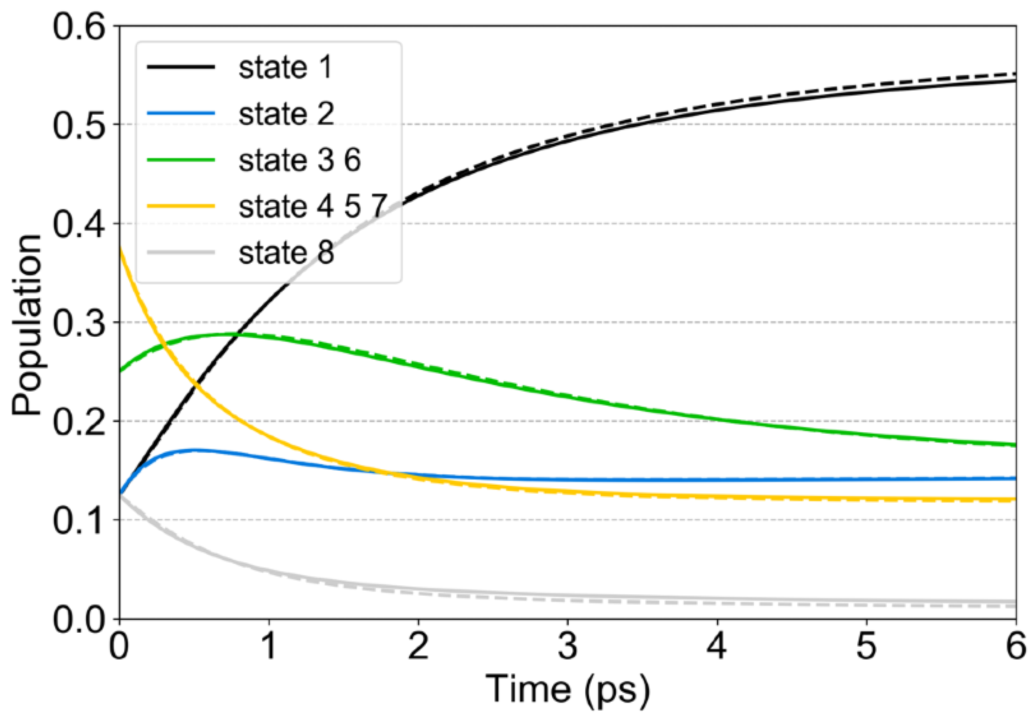
$$\text{distance } d_{ij} \equiv \frac{1}{\max(r_{ji}, r_{ij})}$$

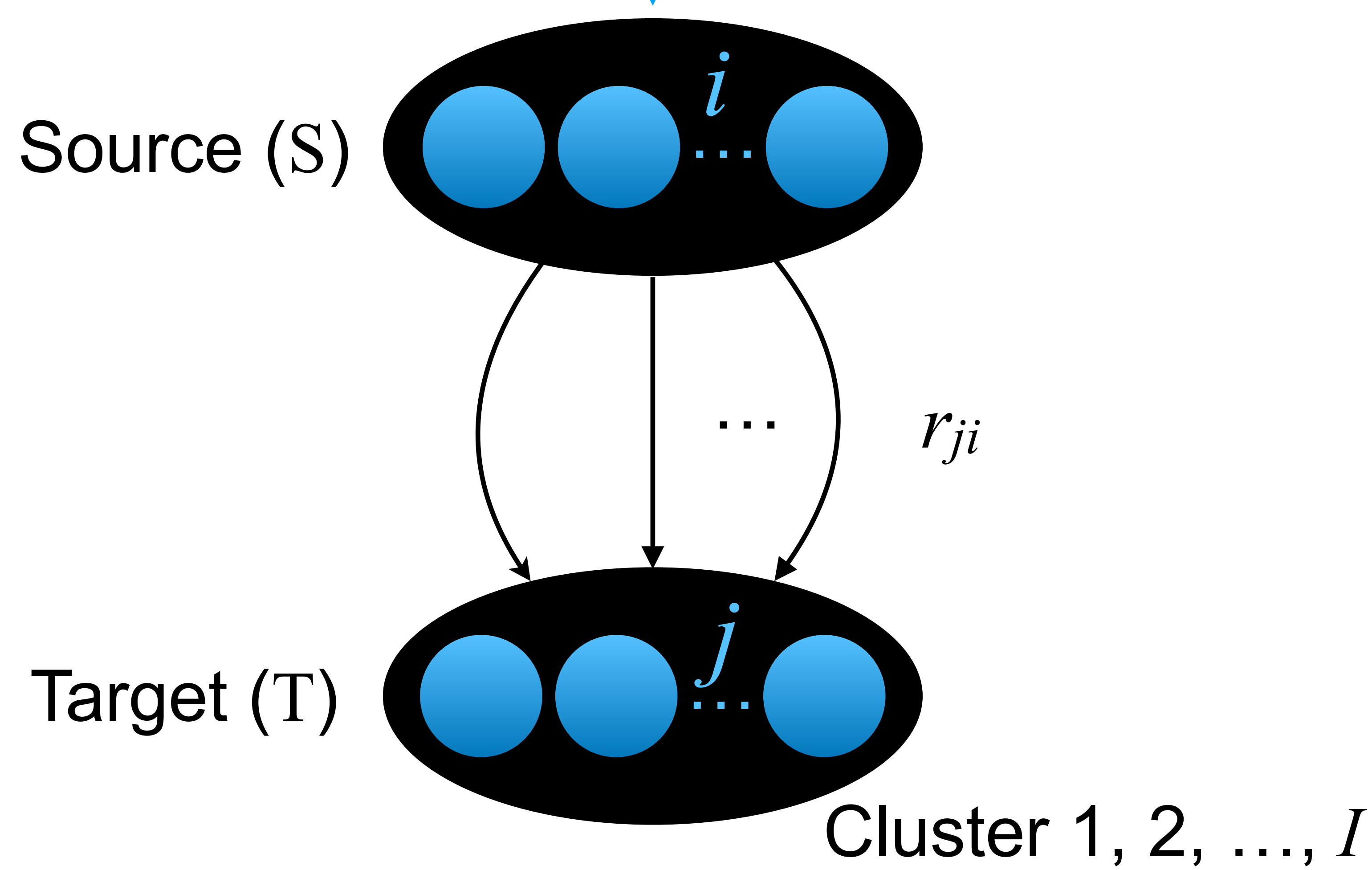
$$\text{variance} \equiv \frac{1}{N^2} \sum_{ij \in S_I} {d_{ij}}^2$$

Reduced Dynamics

Quasi-thermal equilibrium approximation

$$r_{\mathrm{TS}} = \sum_{j \in \mathrm{T}} \sum_{i \in \mathrm{S}} r_{ji} \frac{\exp(-\epsilon_i / k_B T)}{Z_{\mathrm{S}}}$$





With Min-Cut Tree	Top-Down Clustering Method	TDC
	Bottom-Up Clustering Method	BUC
Without Min-Cut Tree	Directly Cut-off Method	DC
	K-Means-like Method	KM

→ **Coarse-Grained Model (CGM)**

$$\mathrm{Cost}(N_c) = \frac{1}{N_c T} \sum_{I}^{N_c} \int_0^T d\tau \left(\mathrm{P}^I_{\mathrm{original}}(\tau) - \mathrm{P}^I_{\mathrm{CGM}}(\tau)\right)^2$$

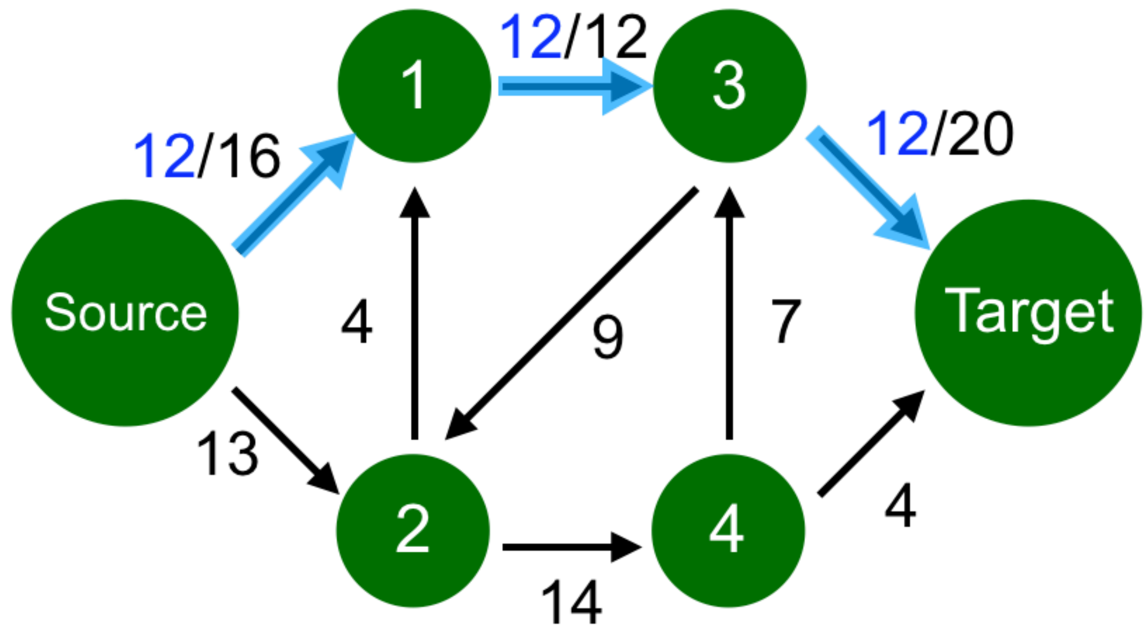
Studying the EET Pathways

- Ford-Fulkerson algorithm:
  - Pathway decompositions
  - Normalized by maximum flow

Maximum flow = 23 → 12/23

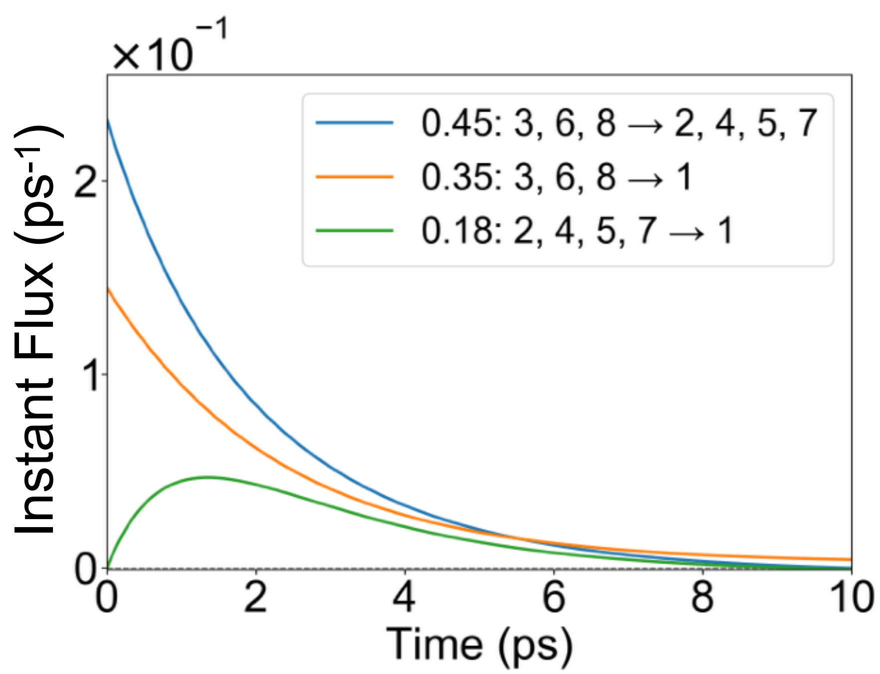
- Markovian dynamics:
  - Time-integrated flux

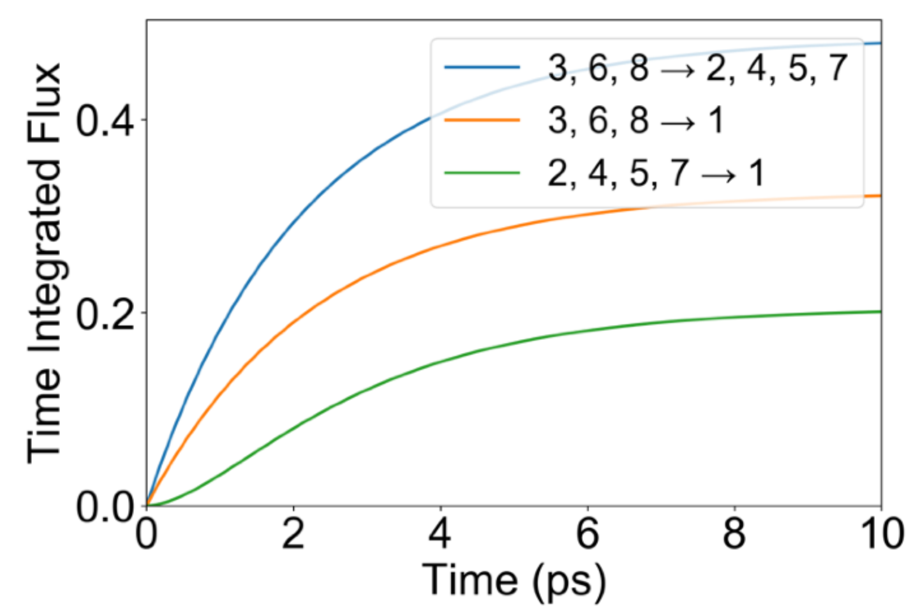
A shortest argument path: a pathway



$$f_{ji}(t) = R_{ji}P_i(t) - R_{ij}P_j(t)$$

$$F_{ji}^{\text{Markovian}}(t) = \int_0^t d\tau f_{ji}(\tau) - f_{ji}(\infty)$$





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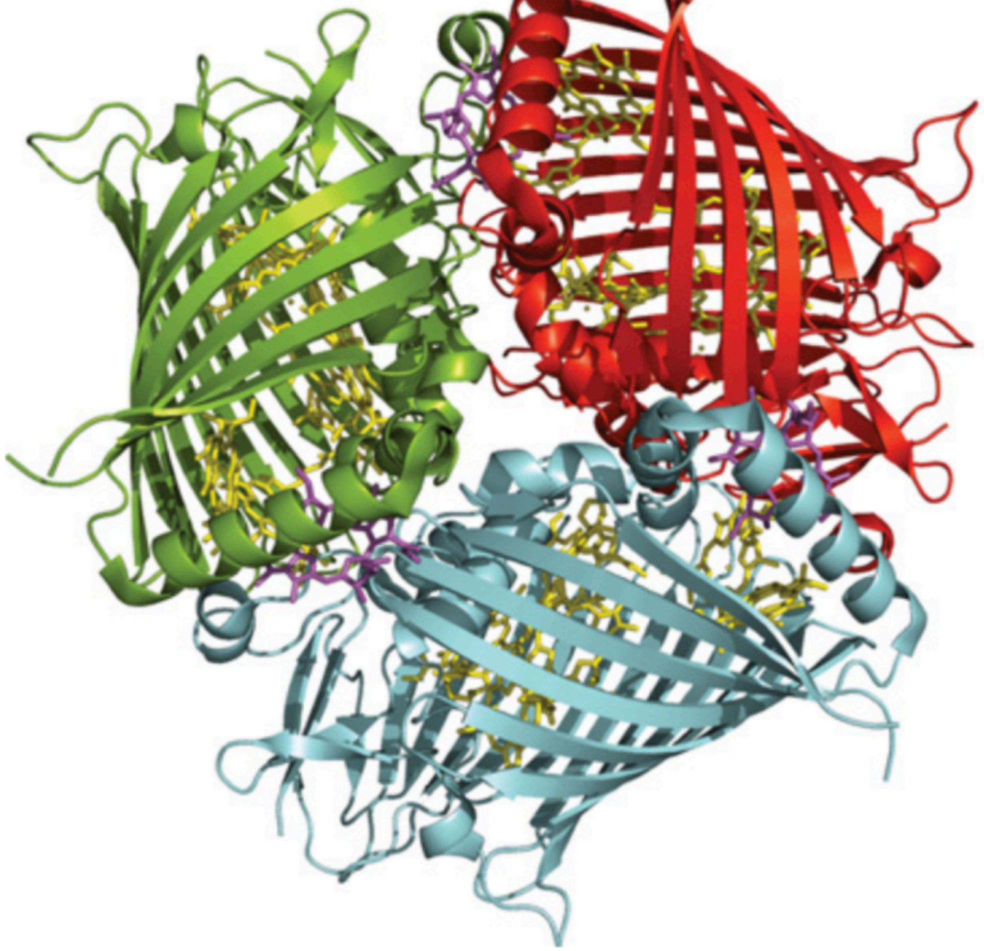
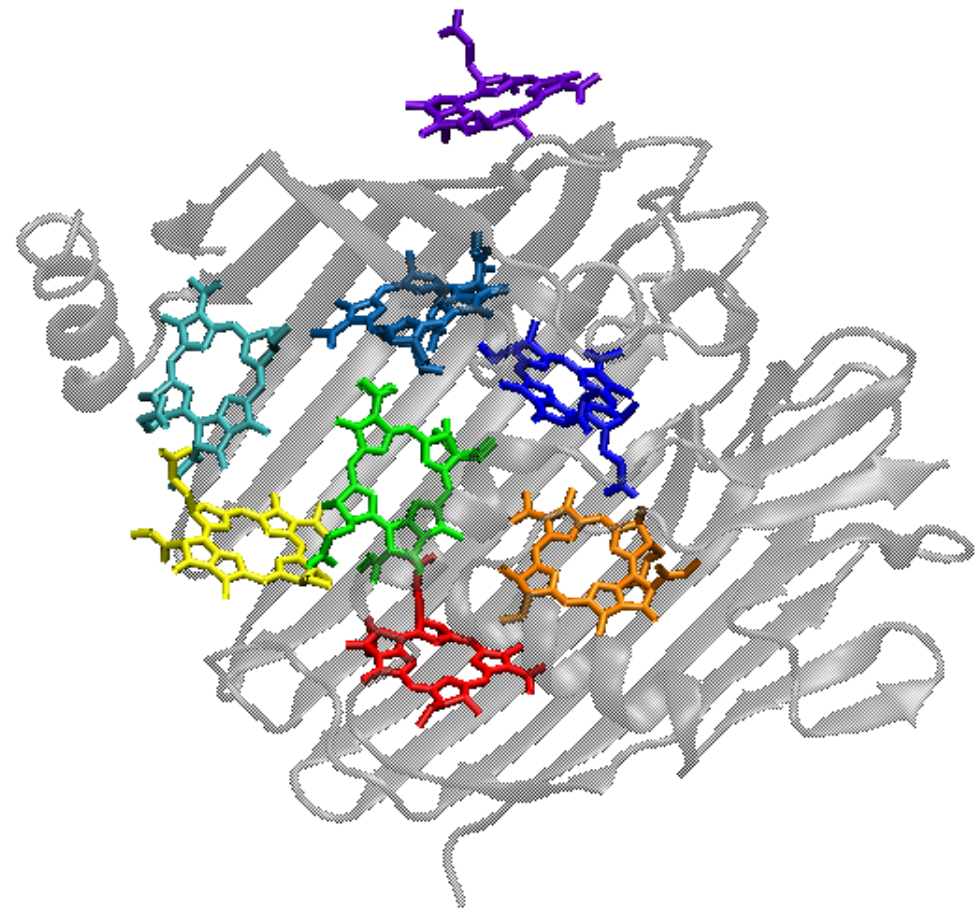
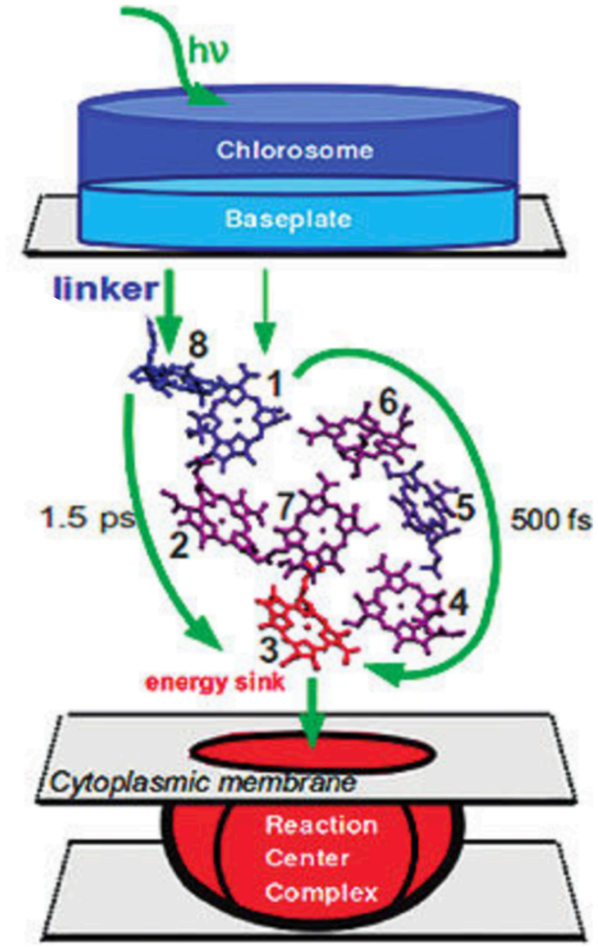
8-Site Fenna-Matthews-Olson (FMO) Complex

- A "funnel" between the reaction center and the antenna system in green sulfur bacteria
- Sites: 8 BChl *a*

PDB: 3EOJ

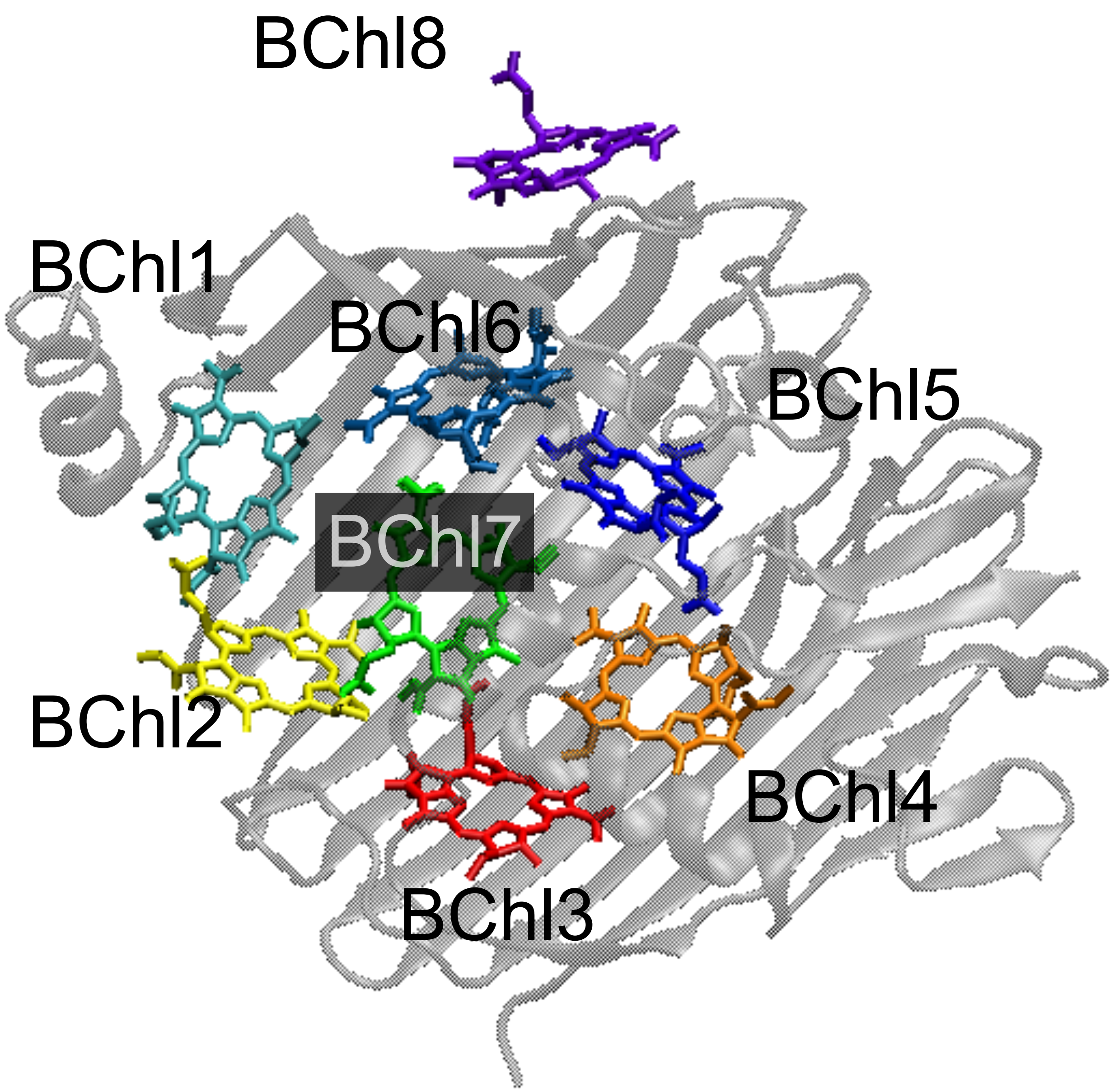


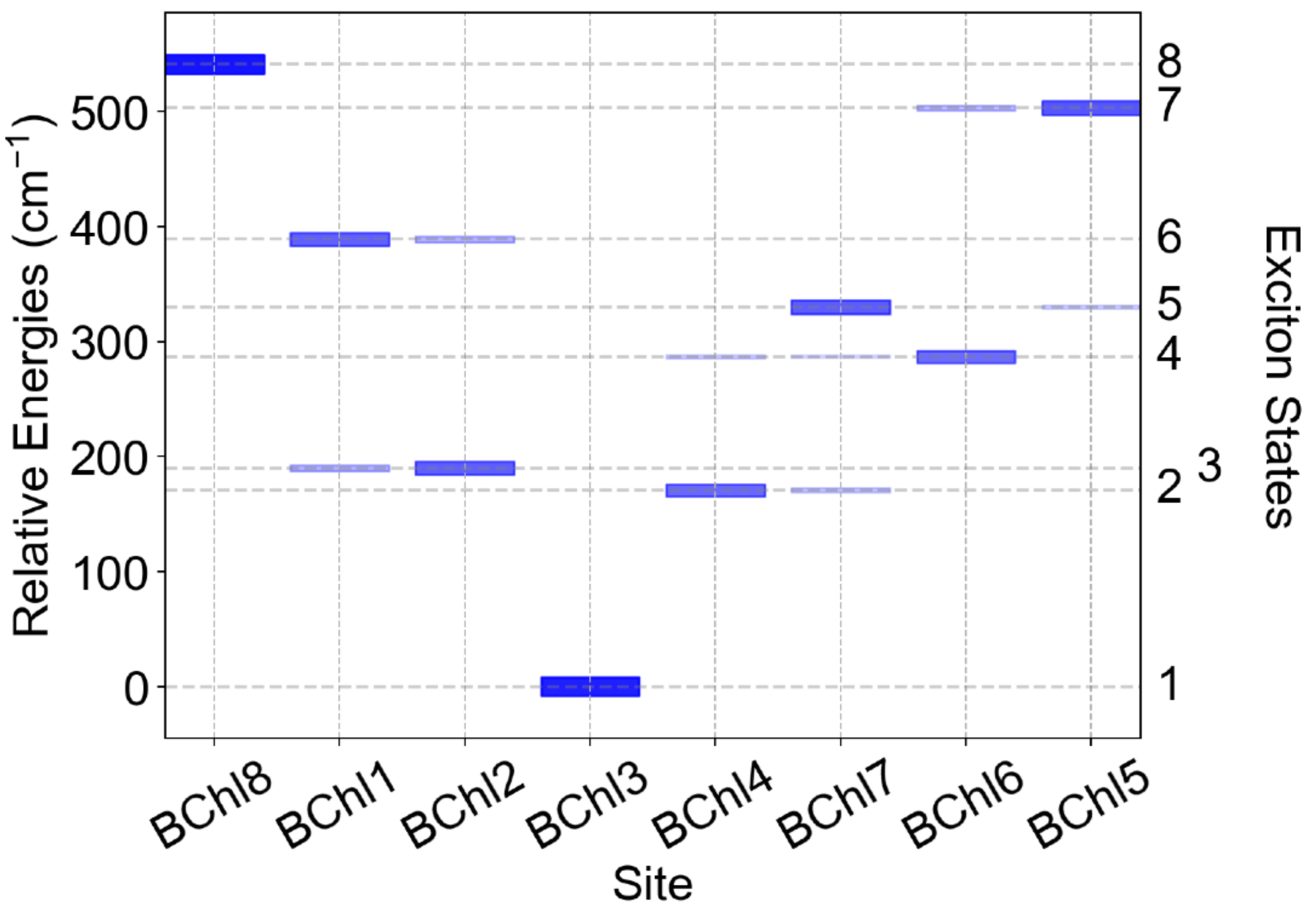




Tronrud, D. E. et al. *Photosynth. Res.* **2009**, *100*, 79
Schmidt Am Busch, M. et al. *JPC L* **2011**, *2*, 93

Exciton Structures of the FMO Complex

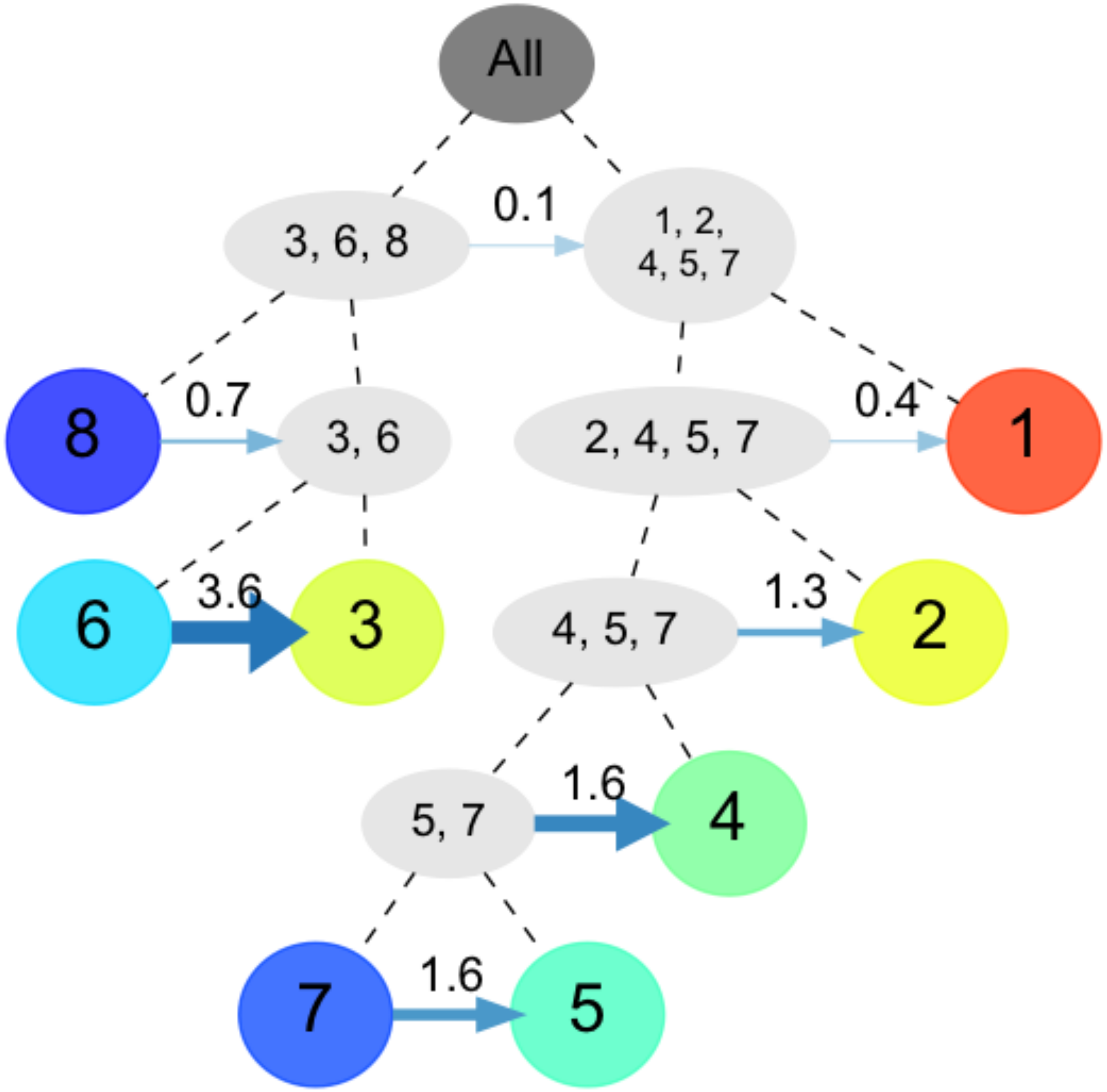




Effective Hamiltonian: Schmidt Am Busch, M. et al. *JPC L* **2011**, *2*, 93

FMO Complex: Tree

- Highest exciton state to lowest exciton state

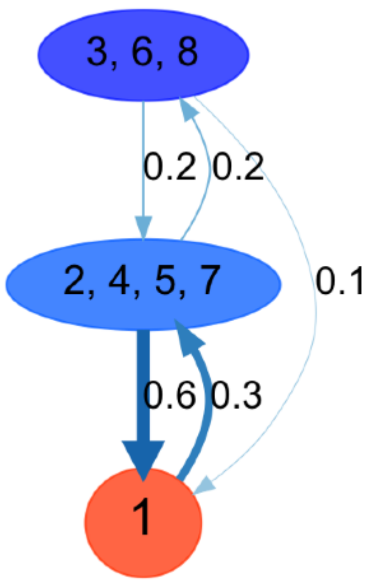


Unit: ps^{-1}

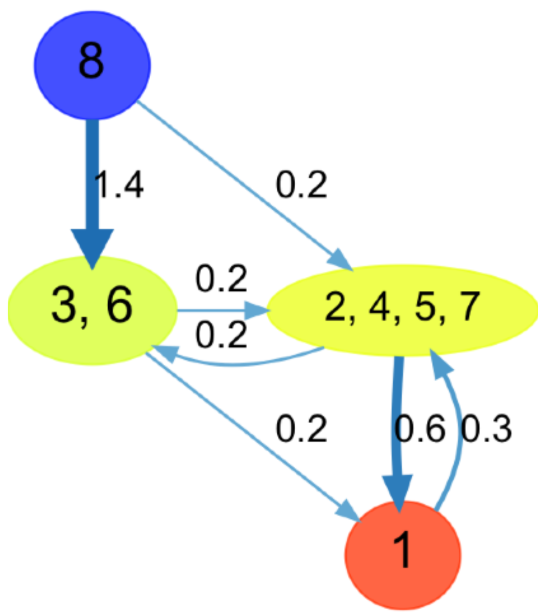
Parameters for modified Redfield theory: Wu, J. et al *JPCL* **2015**, *6*, 1240

FMO Complex: CGM's and Costs

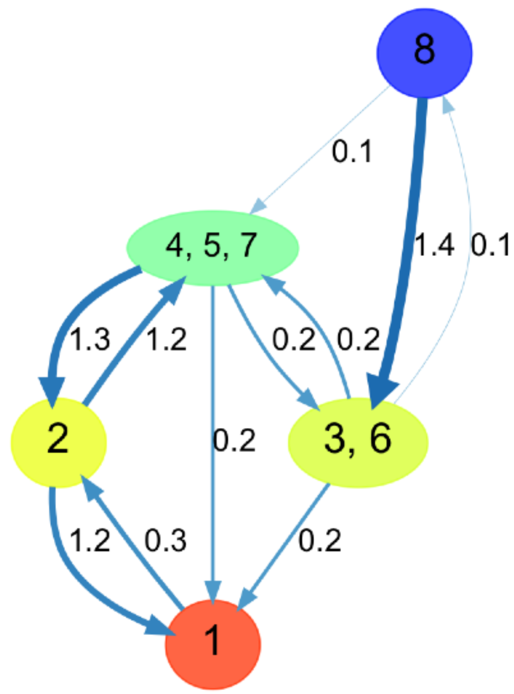
TDC, BUC 3



All 4



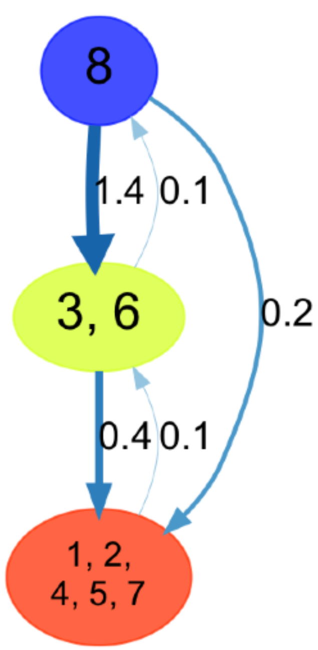
TDC, BUC 5



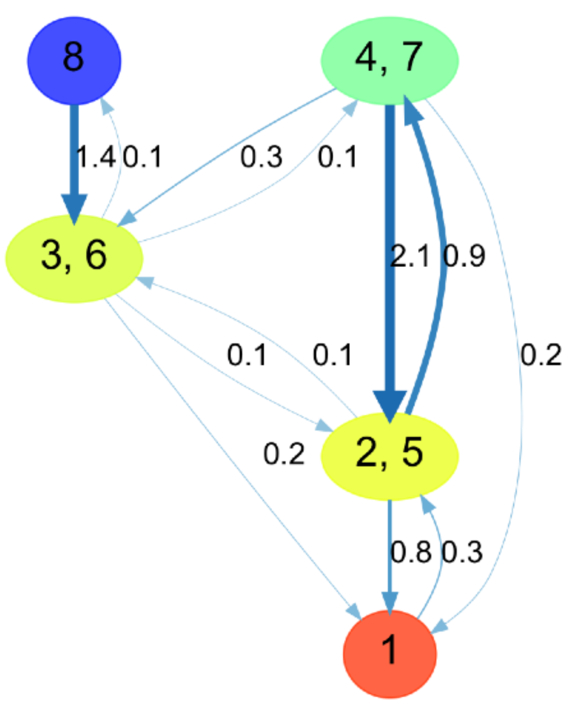
Label: rate (ps^{-1})

$$\mathrm{Cost}(N_c) = \frac{1}{N_c T}\sum_{I}^{N_c}\int_0^T d\tau (\mathrm{P}^I_{\mathrm{original}}(\tau) - \mathrm{P}^I_{\mathrm{CGM}}(\tau))^2$$

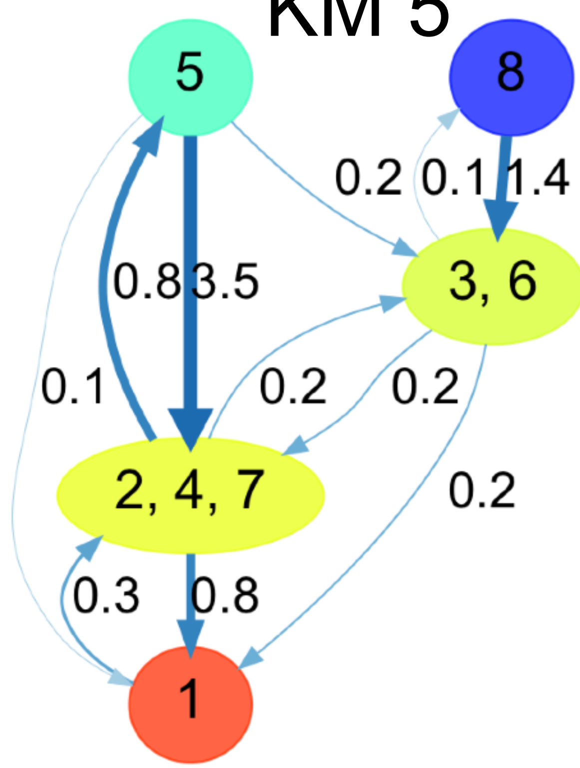
KM, DC 3

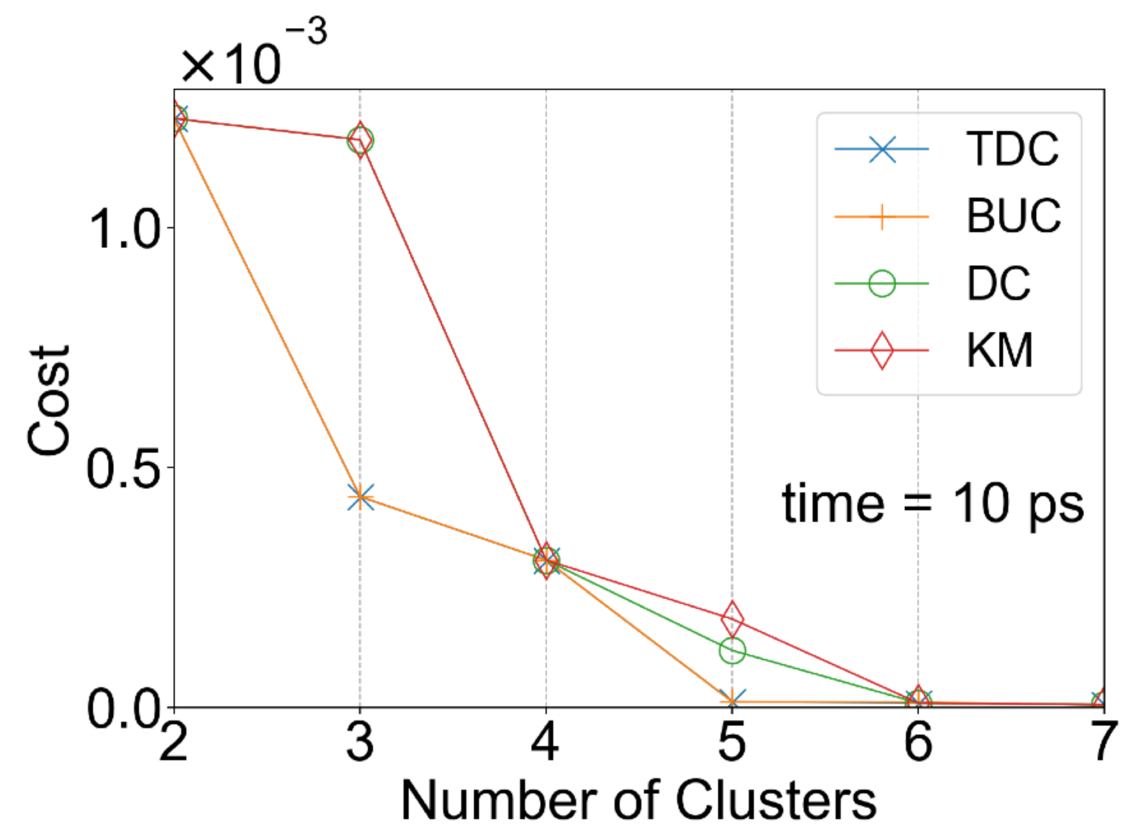


DC 5



KM 5

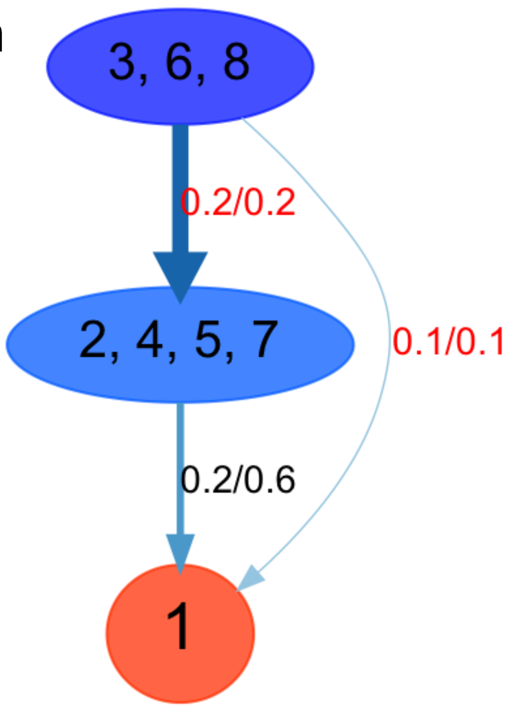


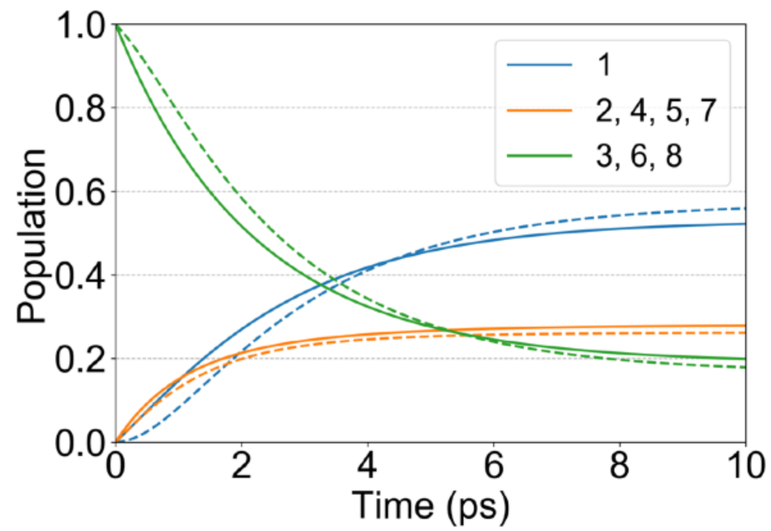


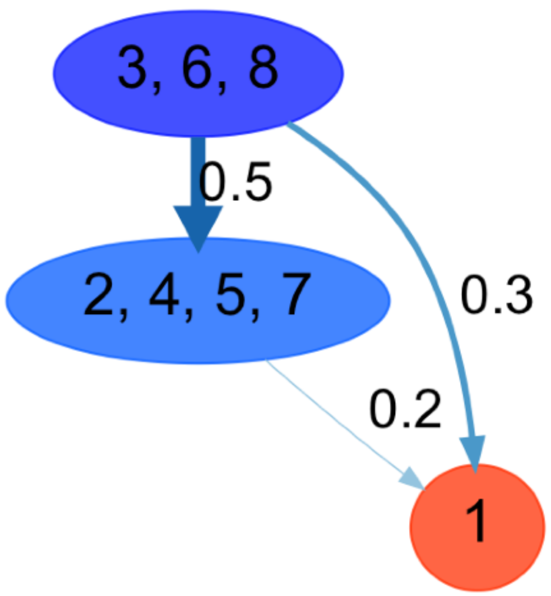
3-Cluster CGM

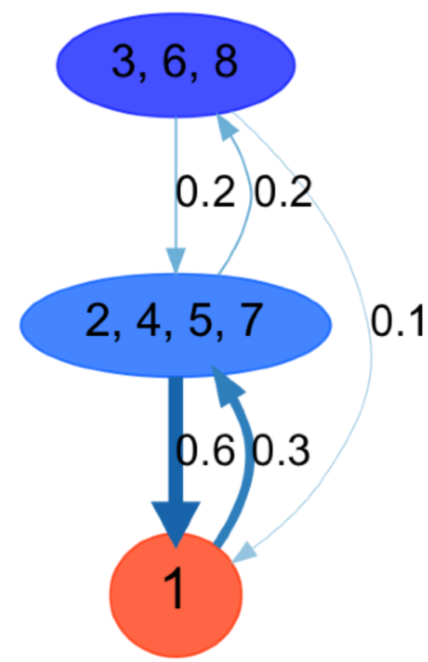
Min Cut | Dynamics | Integrated Flux | Rate

8th

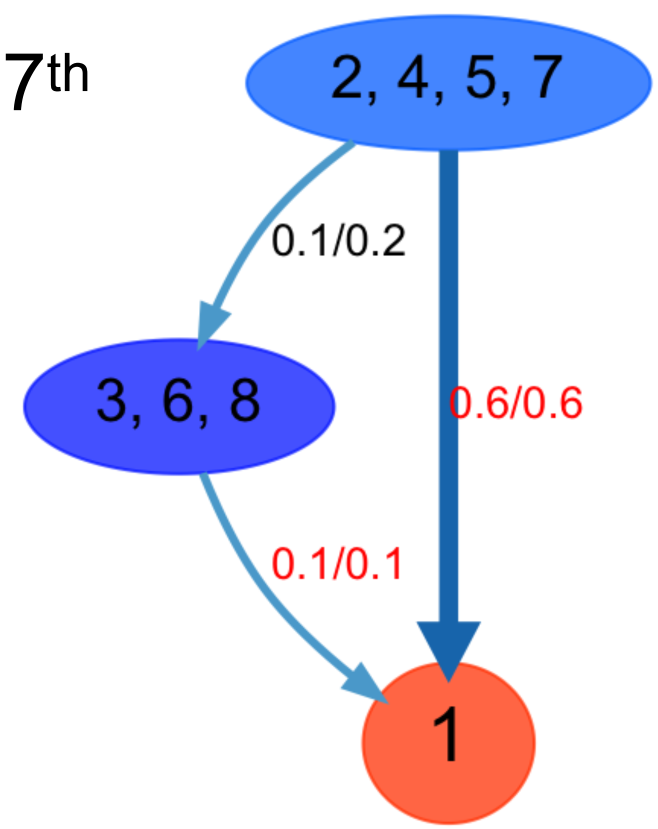


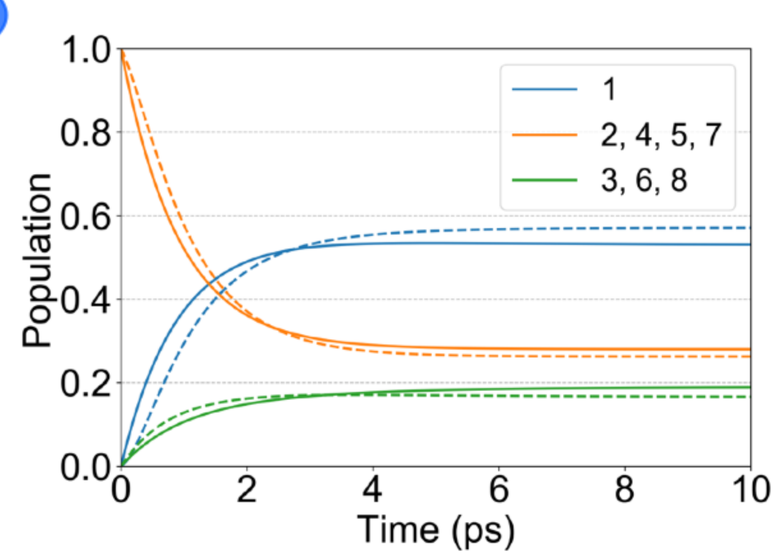


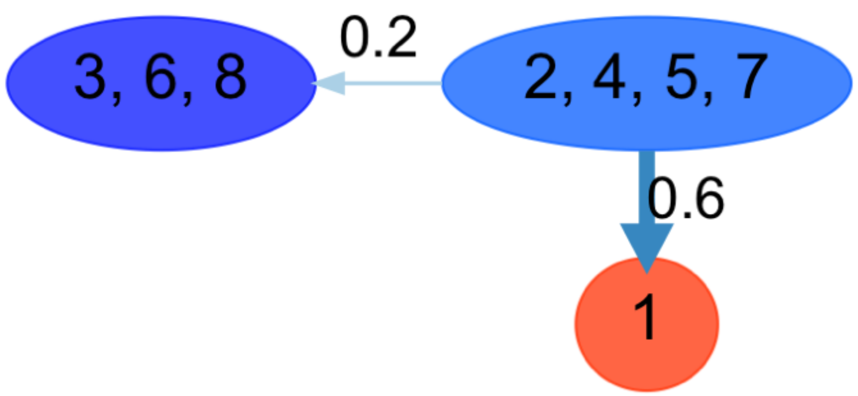




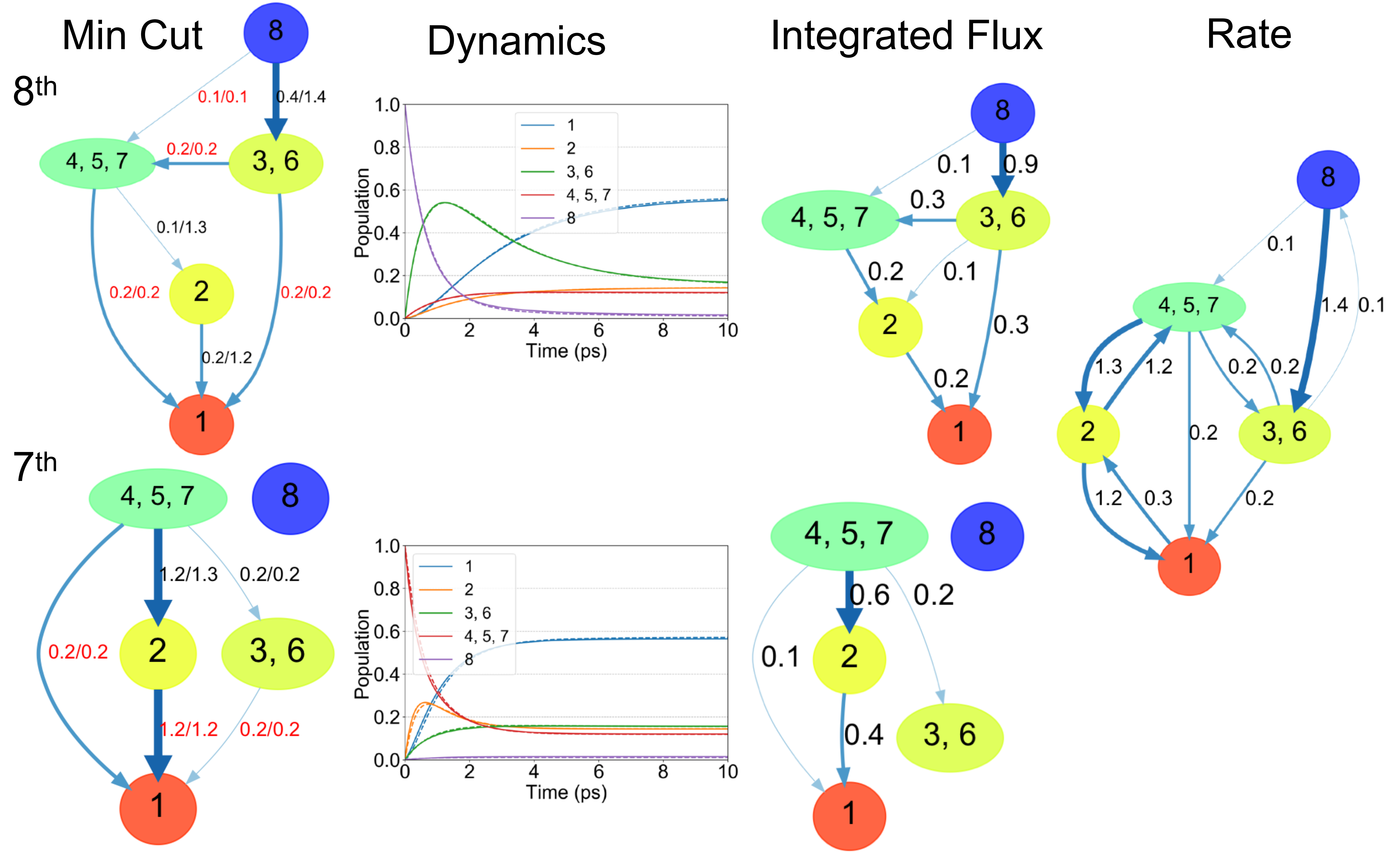
7th







5-Cluster CGM

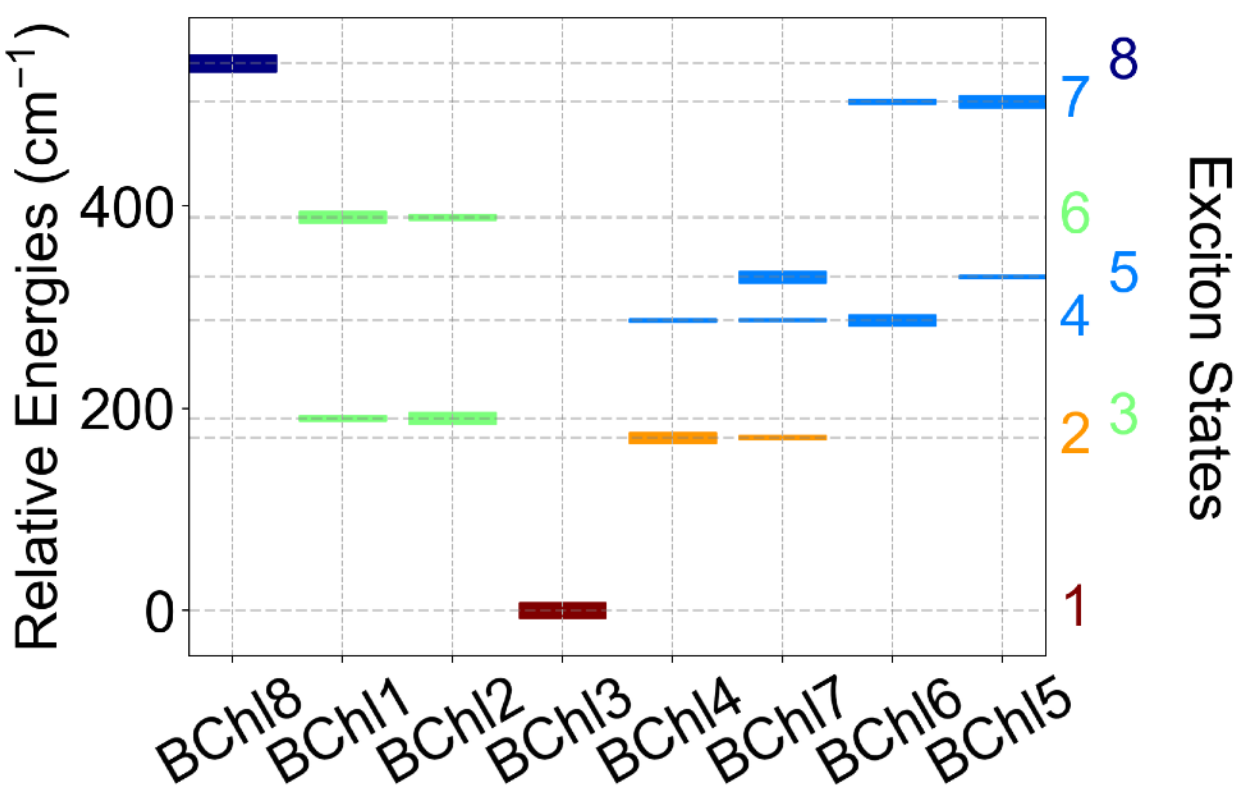


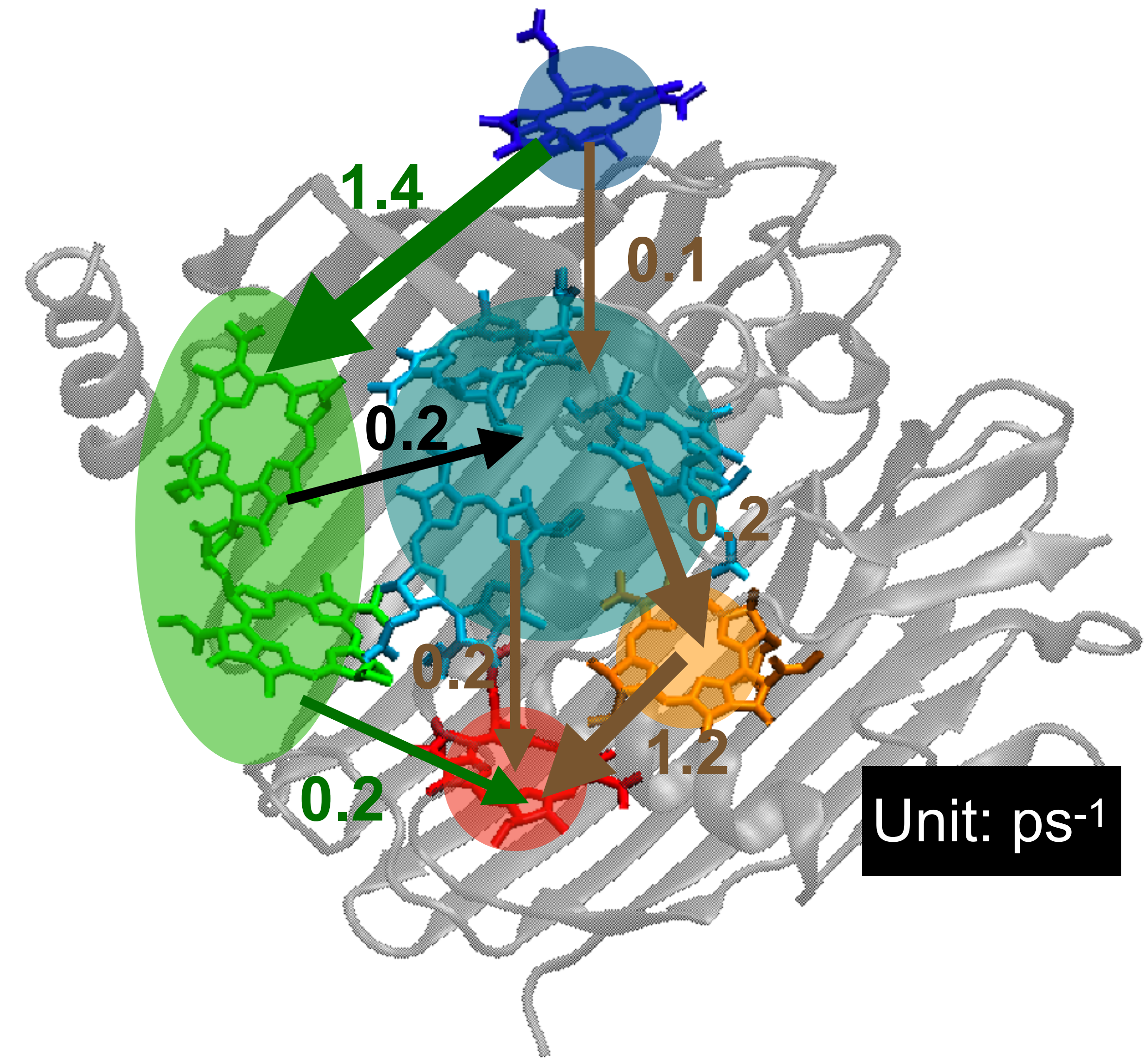
5-Cluster CGM

FFA pathway decomposition:

From 8 to 1:
29%: 8 -> 3,6 -> 1
24%: 8 -> 4,5,7 -> 1
20%: 8 -> 3,6 -> 4,5,7 -> 2 -> 1
12%: 8 -> 3,6 -> 2 -> 1
11%: 8 -> 3,6 -> 4,5,7 -> 1

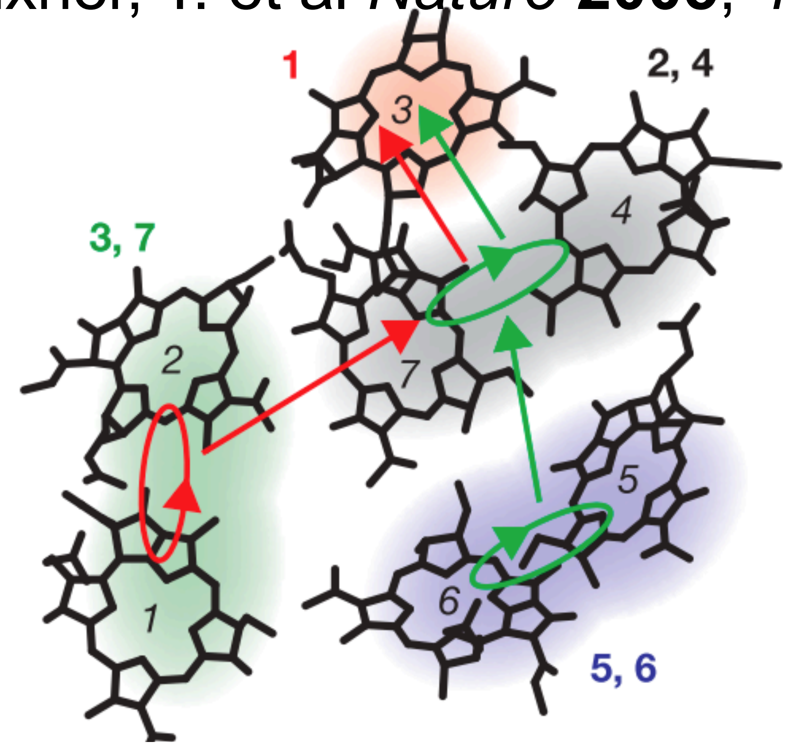
From 7 to 1:
76%: 4,5,7 -> 2 -> 1
13%: 4,5,7 -> 1
11%: 4,5,7 -> 3,6 -> 1

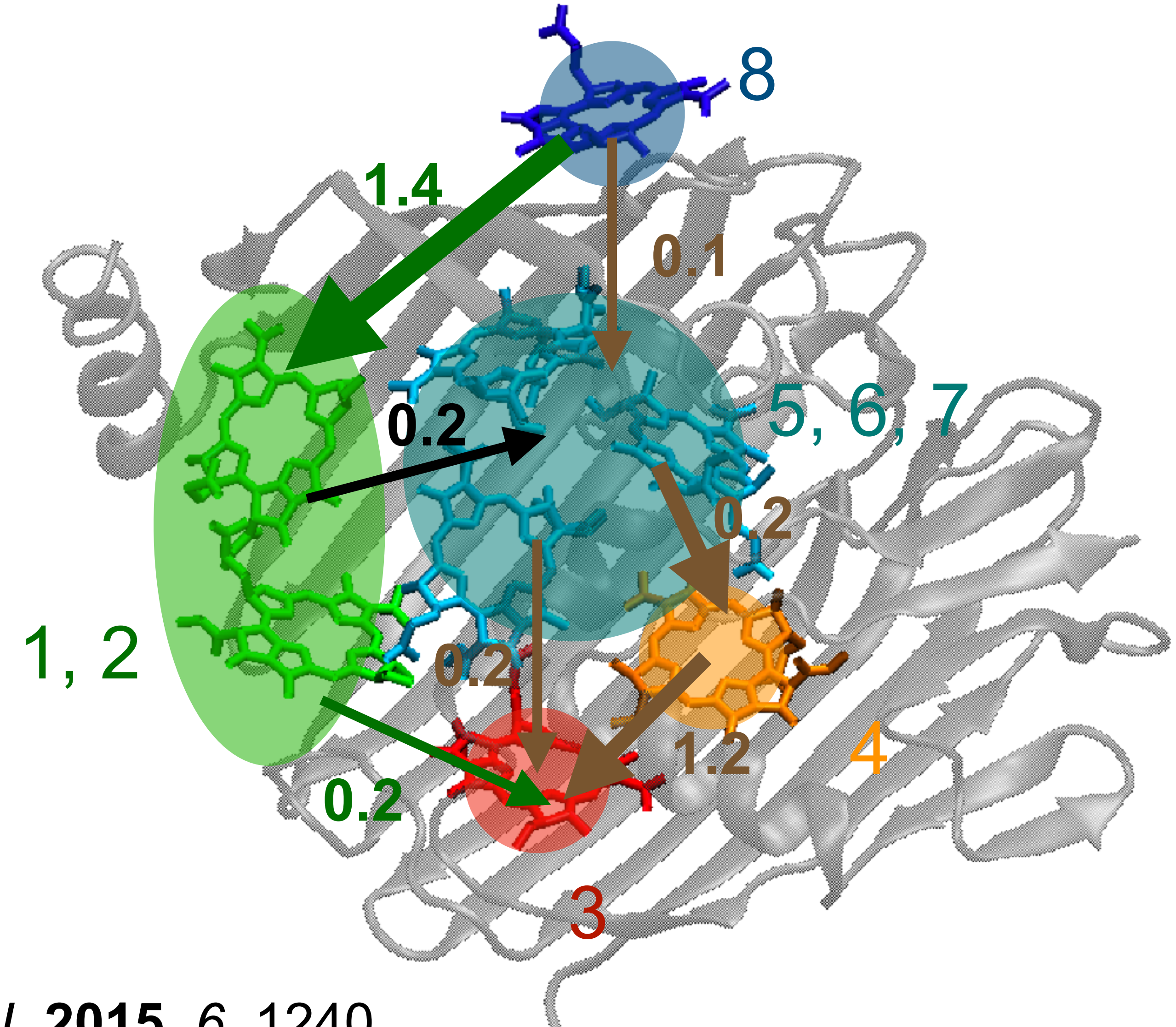




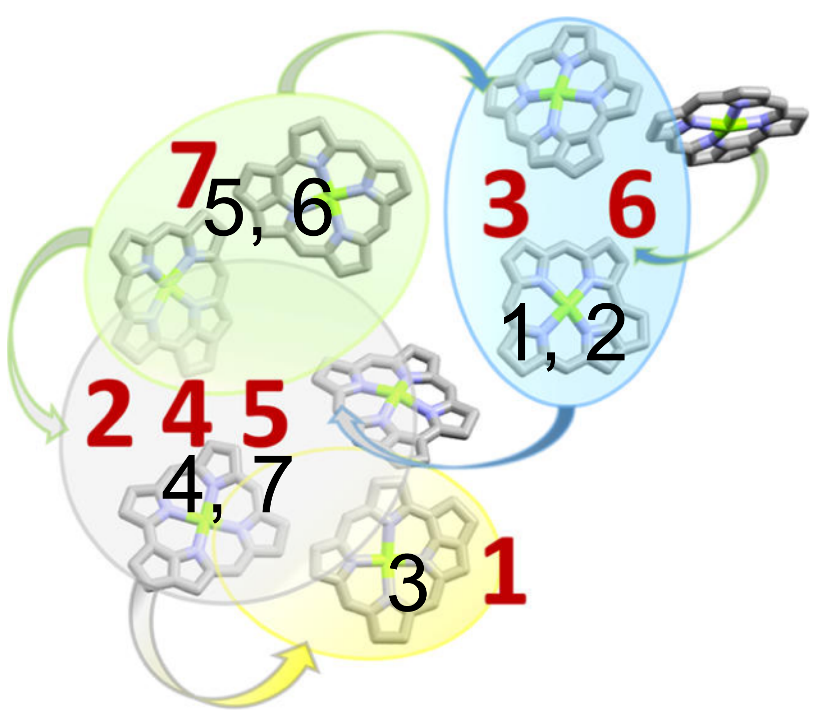
Pathways Comparison

Brixner, T. et al *Nature* **2005**, *434*, 625

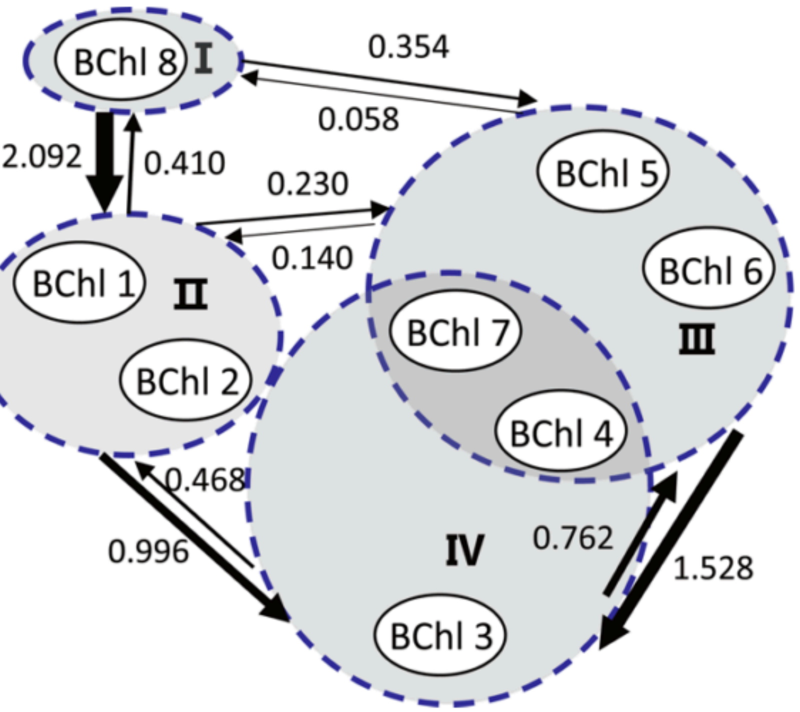




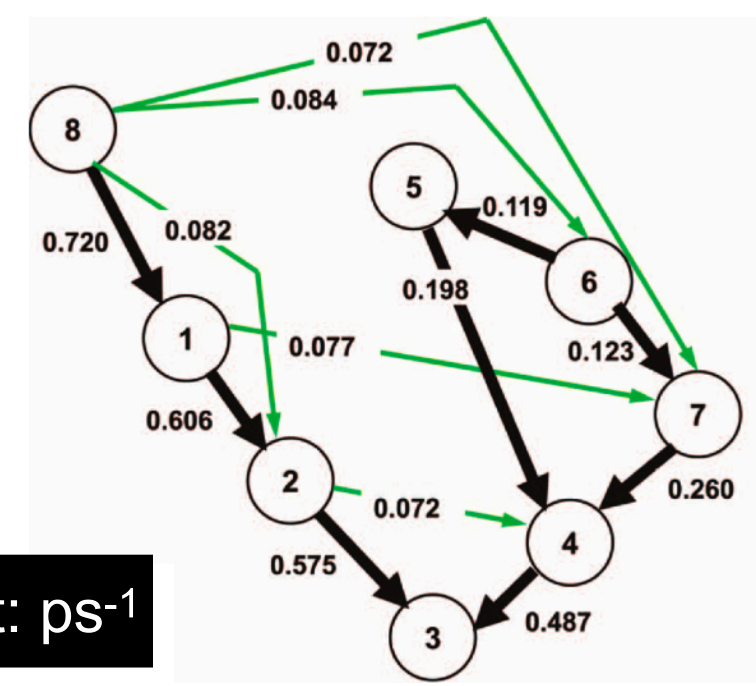
Thyrhaug, E. et al *JPCL* **2016**, *7*, 1653



Wu, J. et al *JPCL* **2015**, *6*, 1240



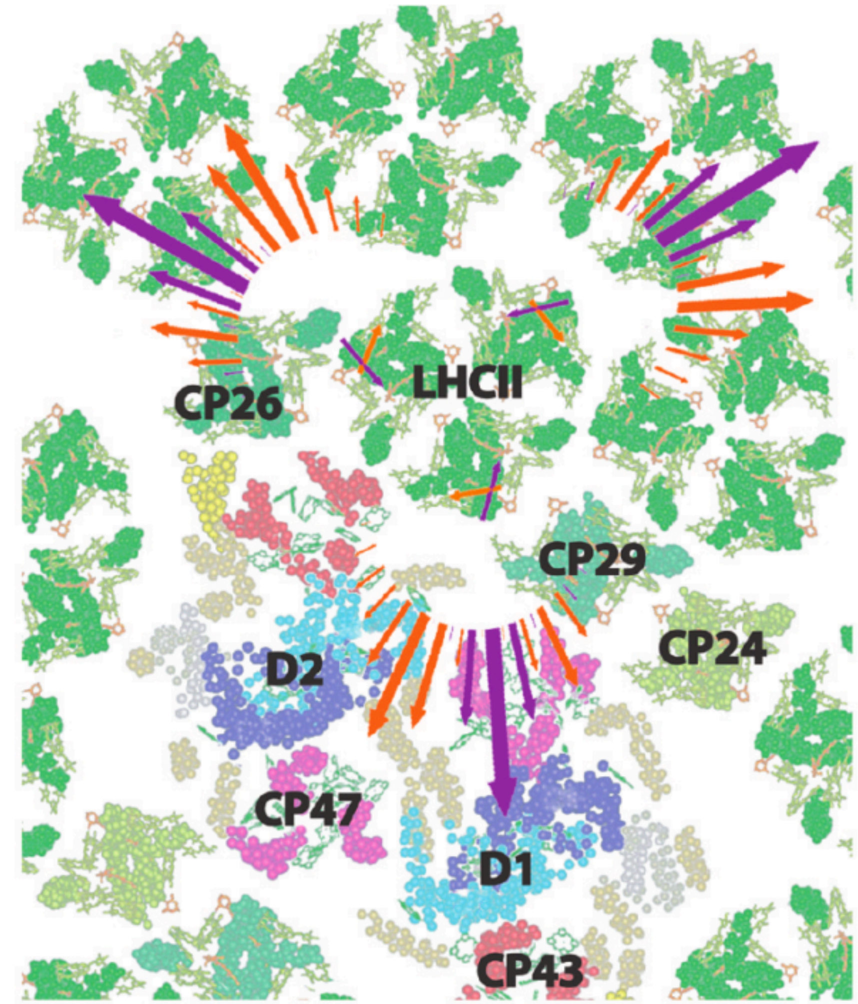
Wu, J. et al *JCP* **2012**, *137*, 174111

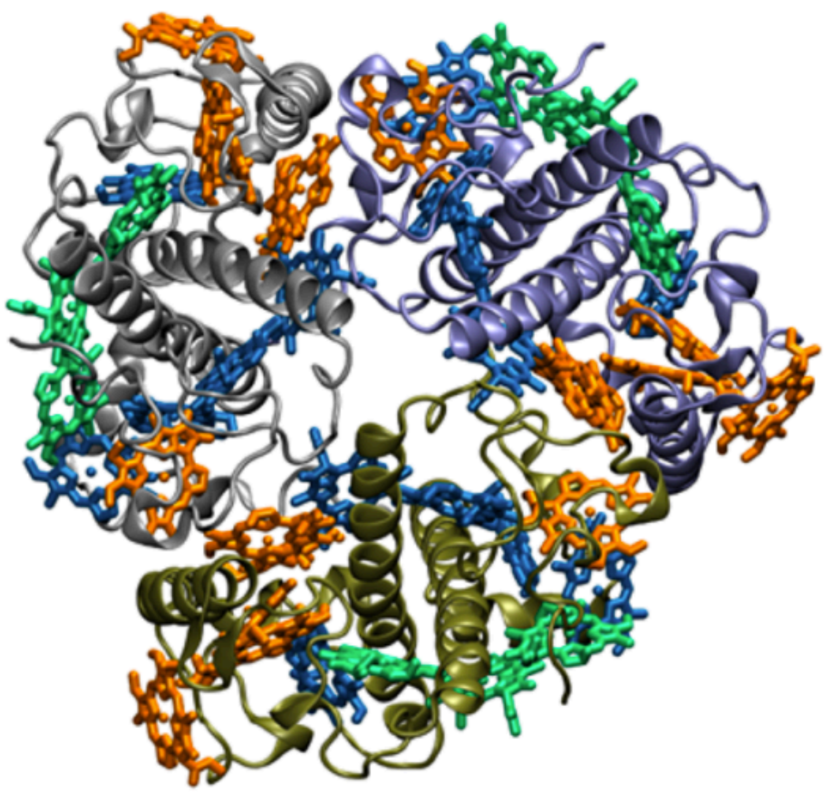


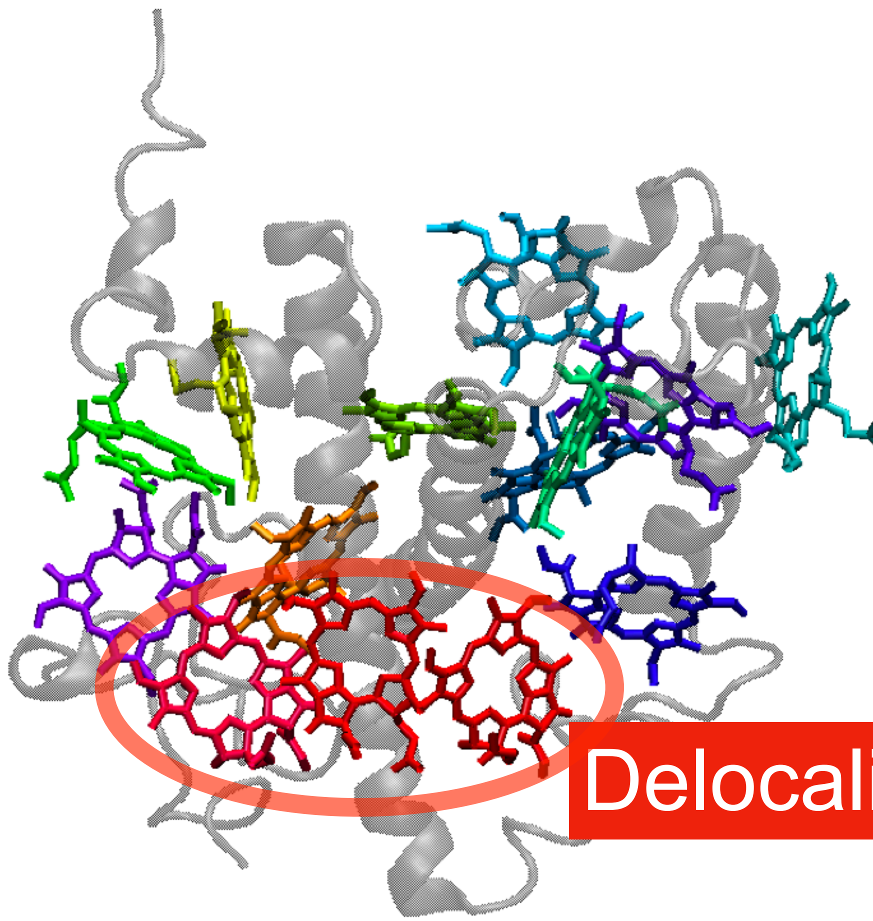
Unit: ps^{-1}

14-Site Light Harvesting Complex II (LHCII) Monomer

- Found in plants and many algae
- Mainly in trimer form
- 14 sites = 8 Chl *a* + 6 Chl *b*



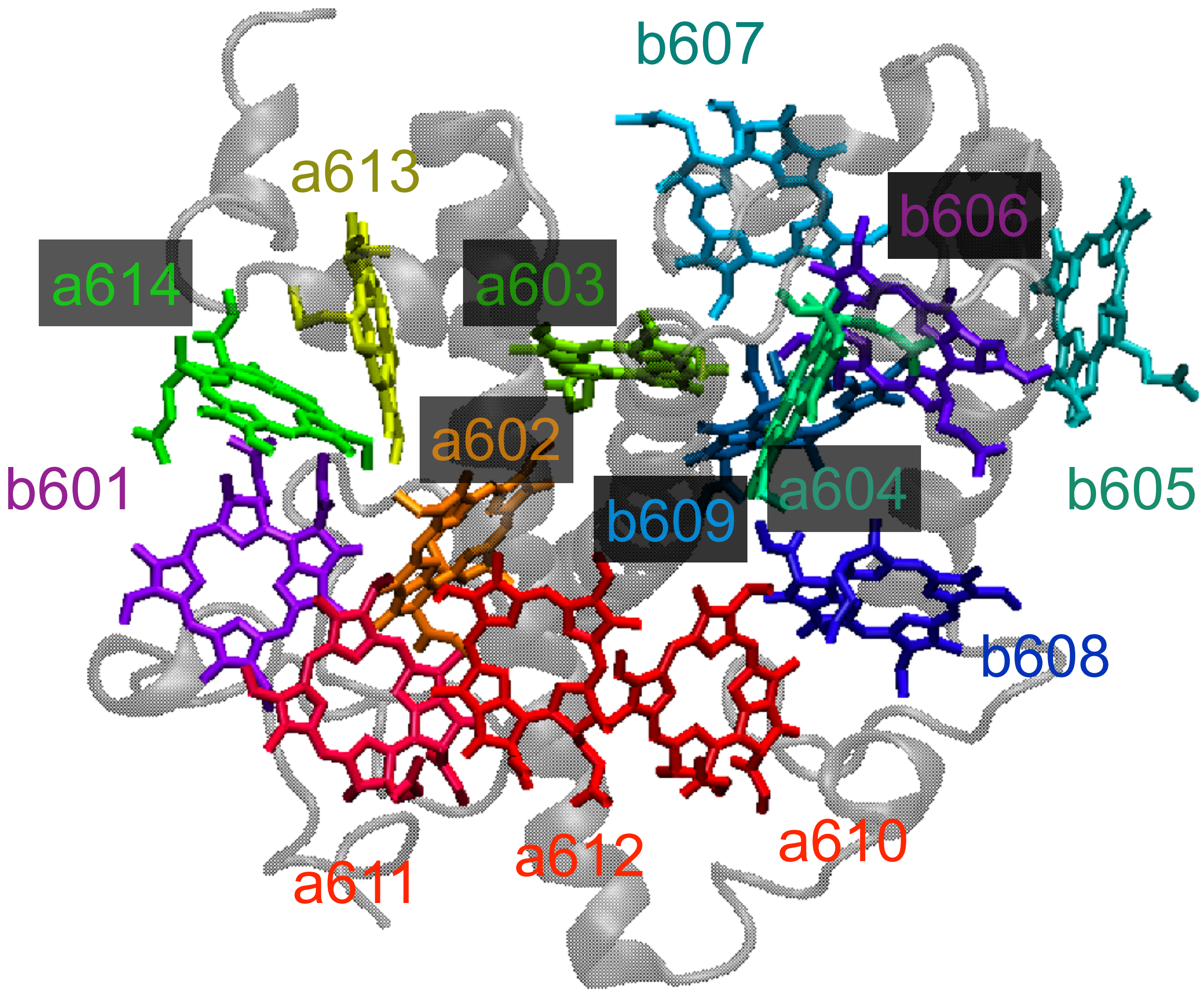


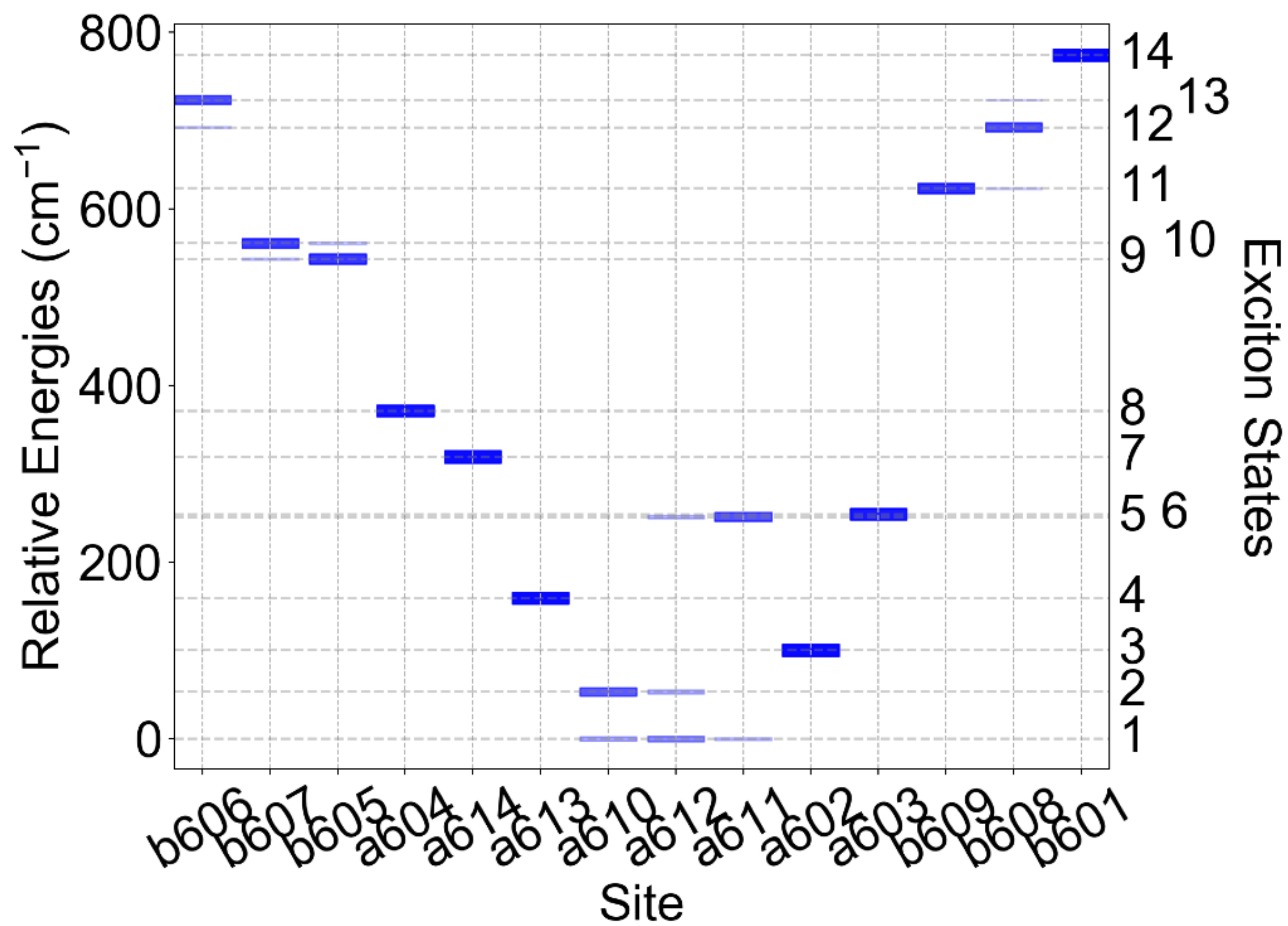


PDB: 1RWT

Liu, Z. *Nature* **2004**, *428*, 287
Curutchet, C. *et al Chem. Rev.* **2017**, *117*, 294
Schlau-Cohen, G. S. et al *JPC B* **2009**, *113*, 15352

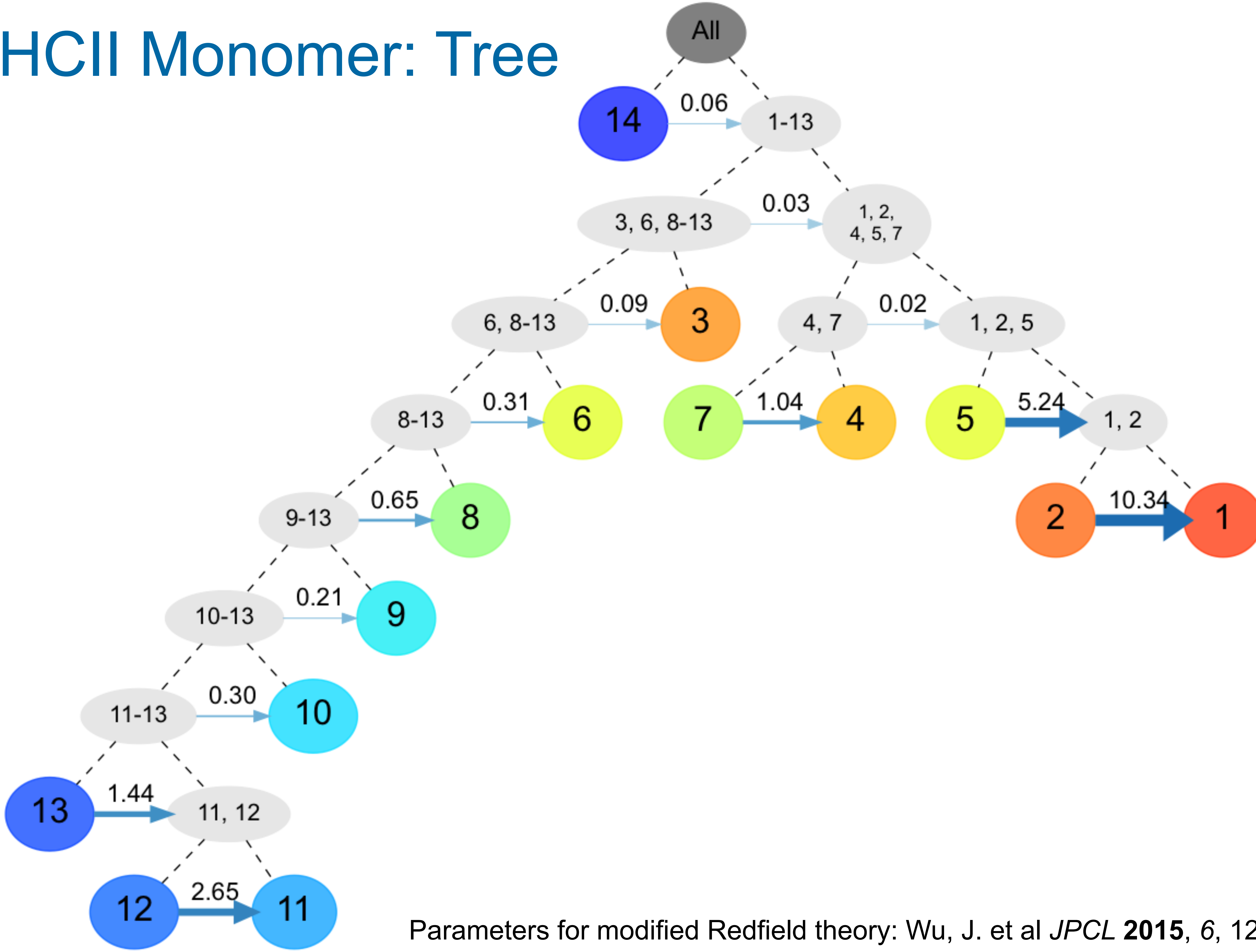
Exciton Structures of the LHCII Monomer





Effective Hamiltonian: Schlau-Cohen, G. S. et al *JPC B* **2009**, *113*, 15352

LHCII Monomer: Tree

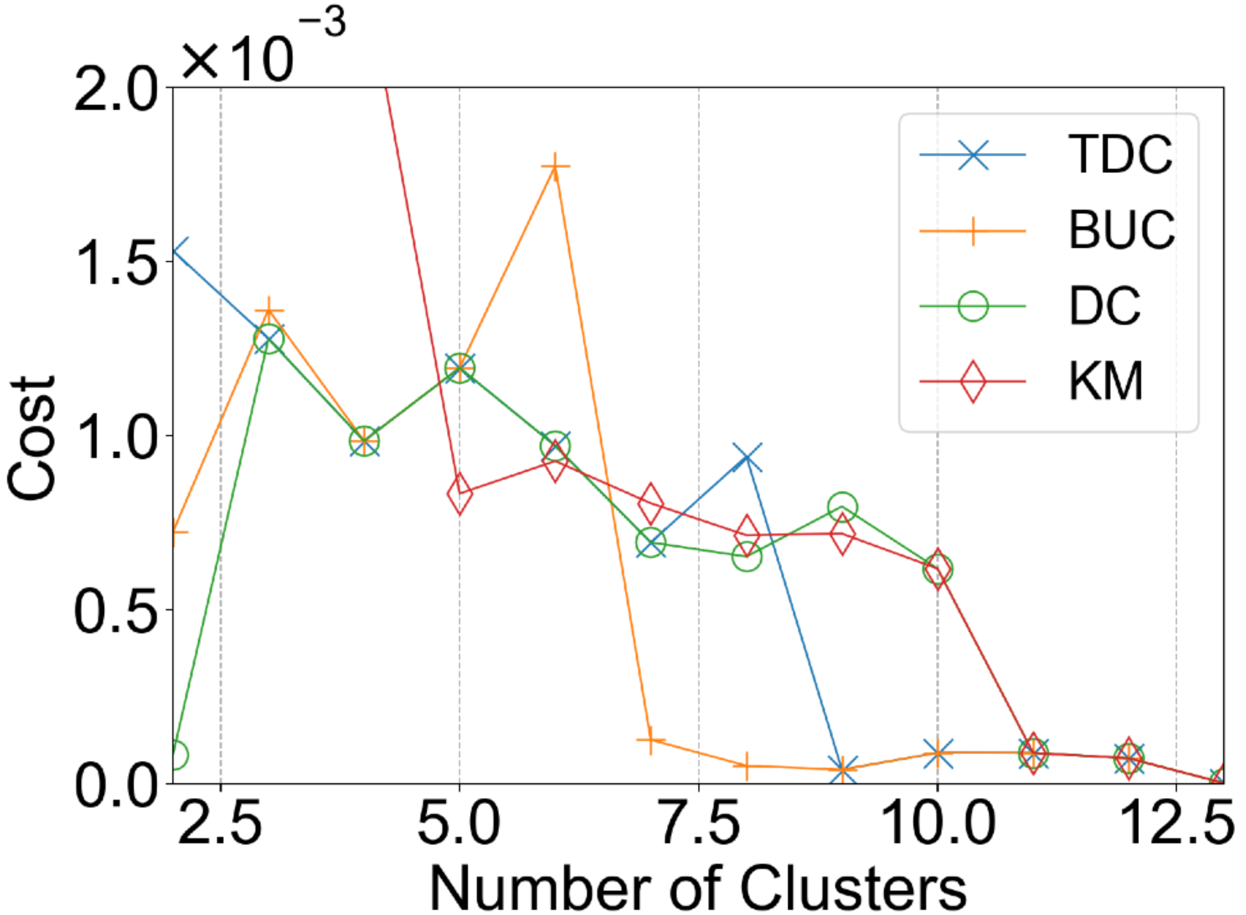


Parameters for modified Redfield theory: Wu, J. et al *JPCL* **2015**, *6*, 1240

LHCII Monomer: Costs

- Sharp decreases in Cost(N_C) are observed when N_C increases from 6 to 7 for BUC, from 8 to 9 for TDC and from 10 to 11 for KM and DC.

$$\mathrm{Cost}(N_c) = \frac{1}{N_c T} \sum_{I}^{N_c} \int_0^T d\tau (\mathrm{P}^I_{\mathrm{original}}(\tau) - \mathrm{P}^I_{\mathrm{CGM}}(\tau))^2$$

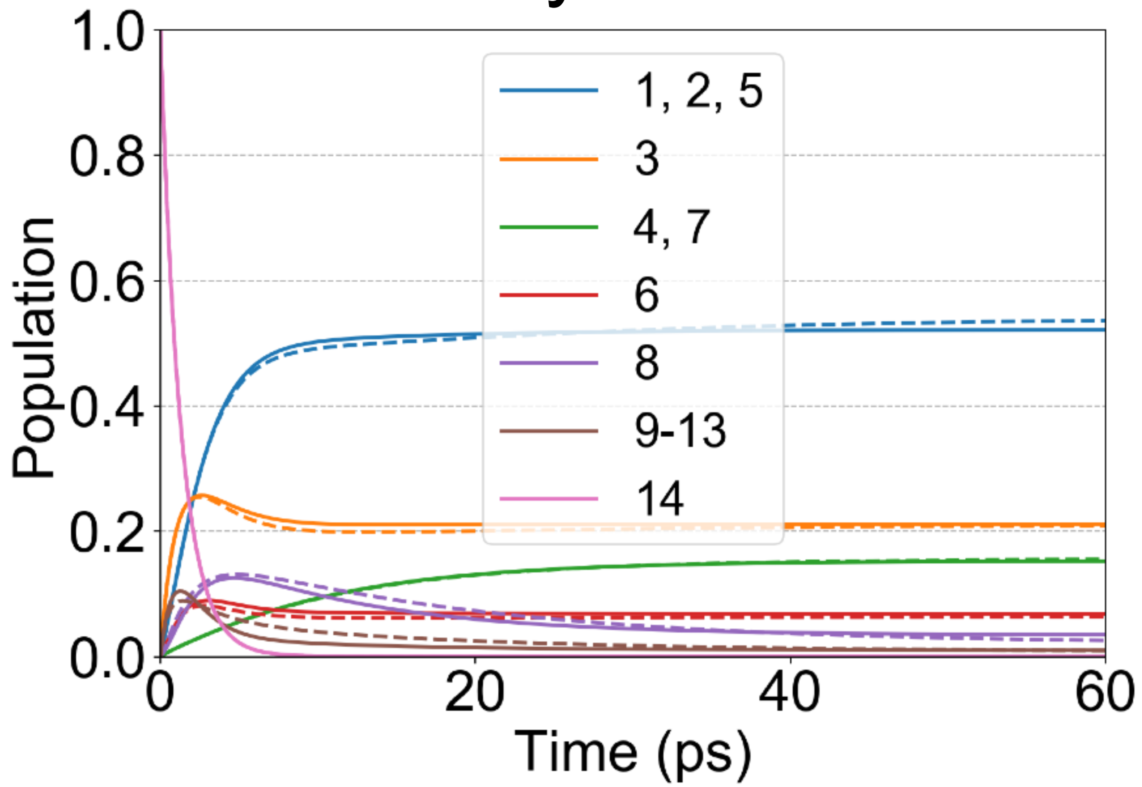


Isolation of 8th state (a604) is crucial!

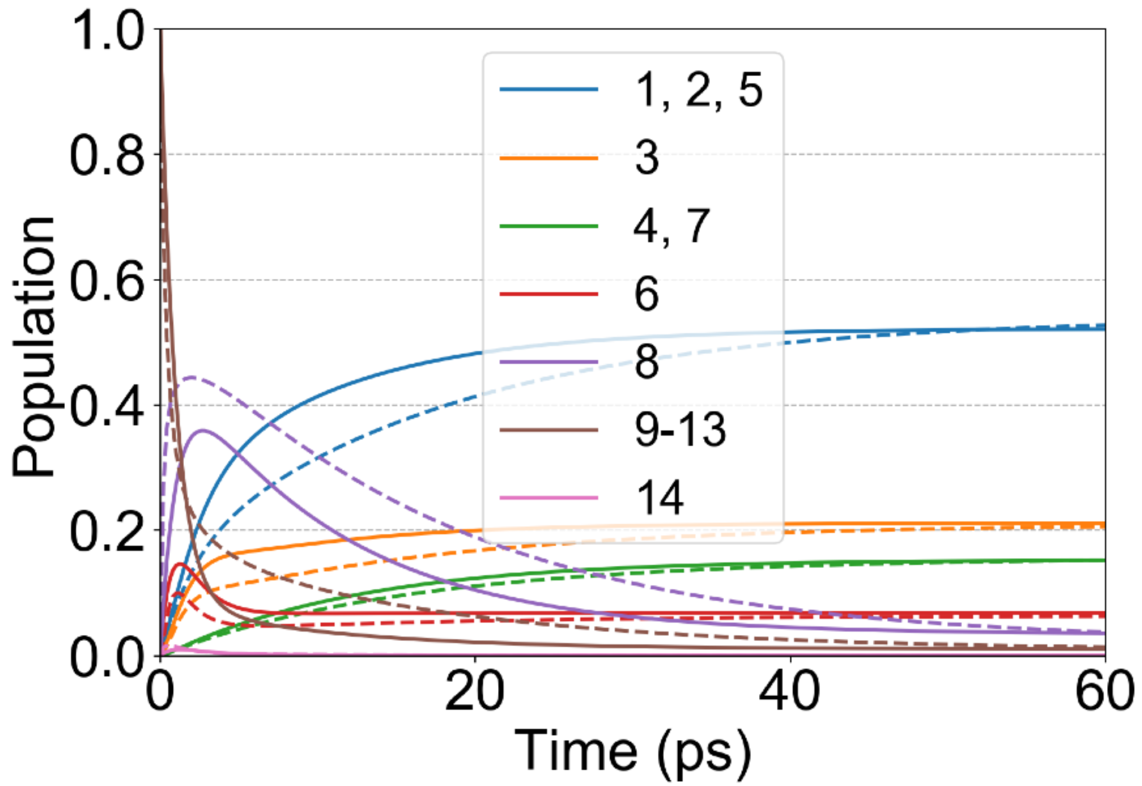
7-cluster BUC CGM

Dynamics

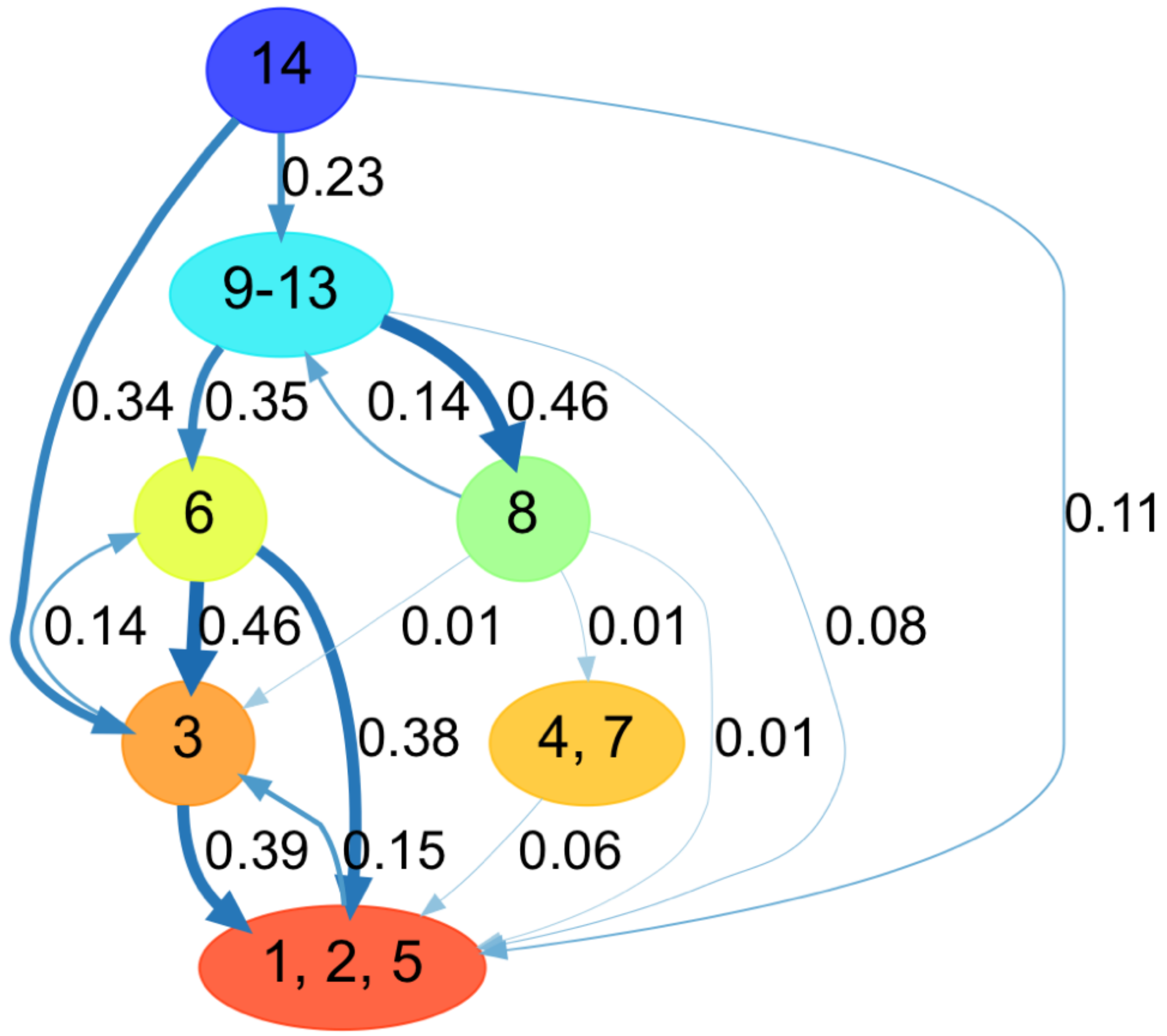
14th



13th



Rate

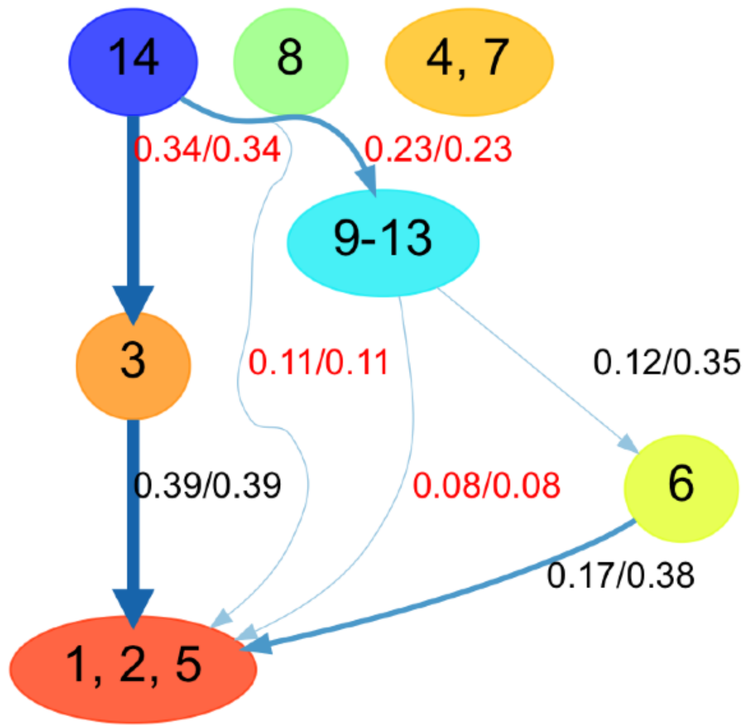


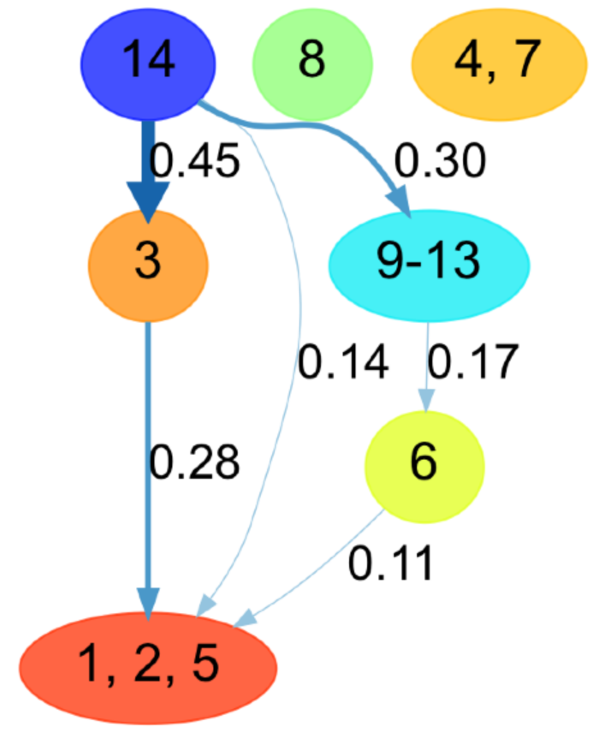
7-cluster BUC CGM

Min Cut

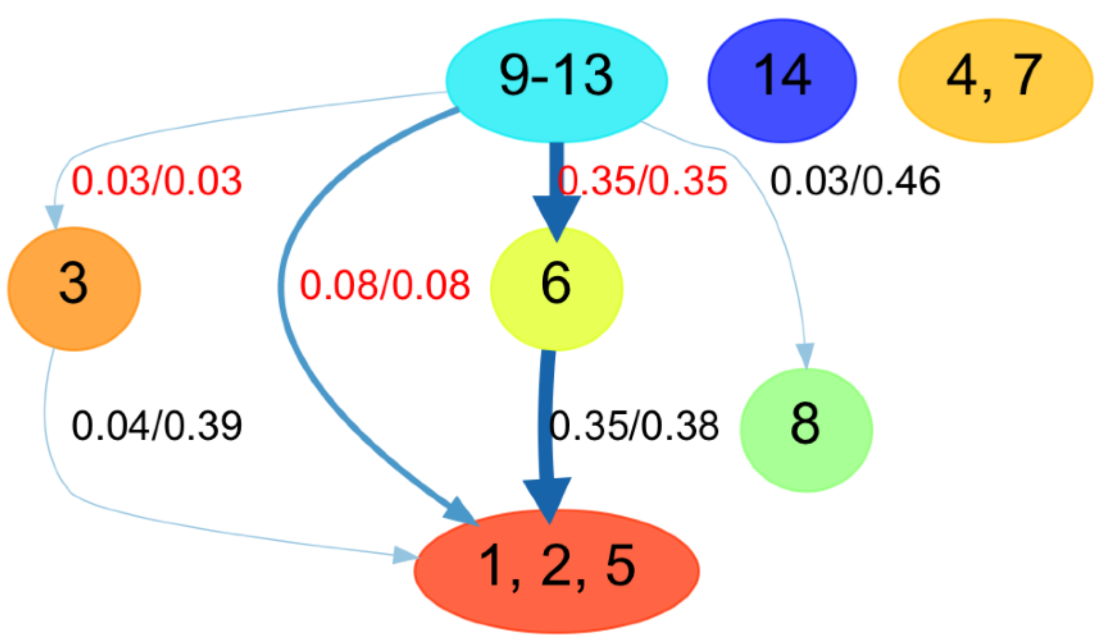
Integrated Flux

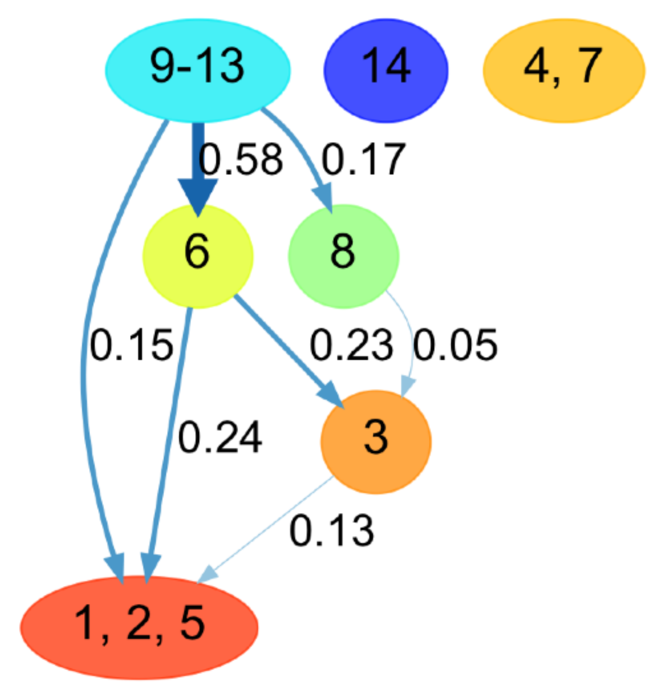
14th





13th



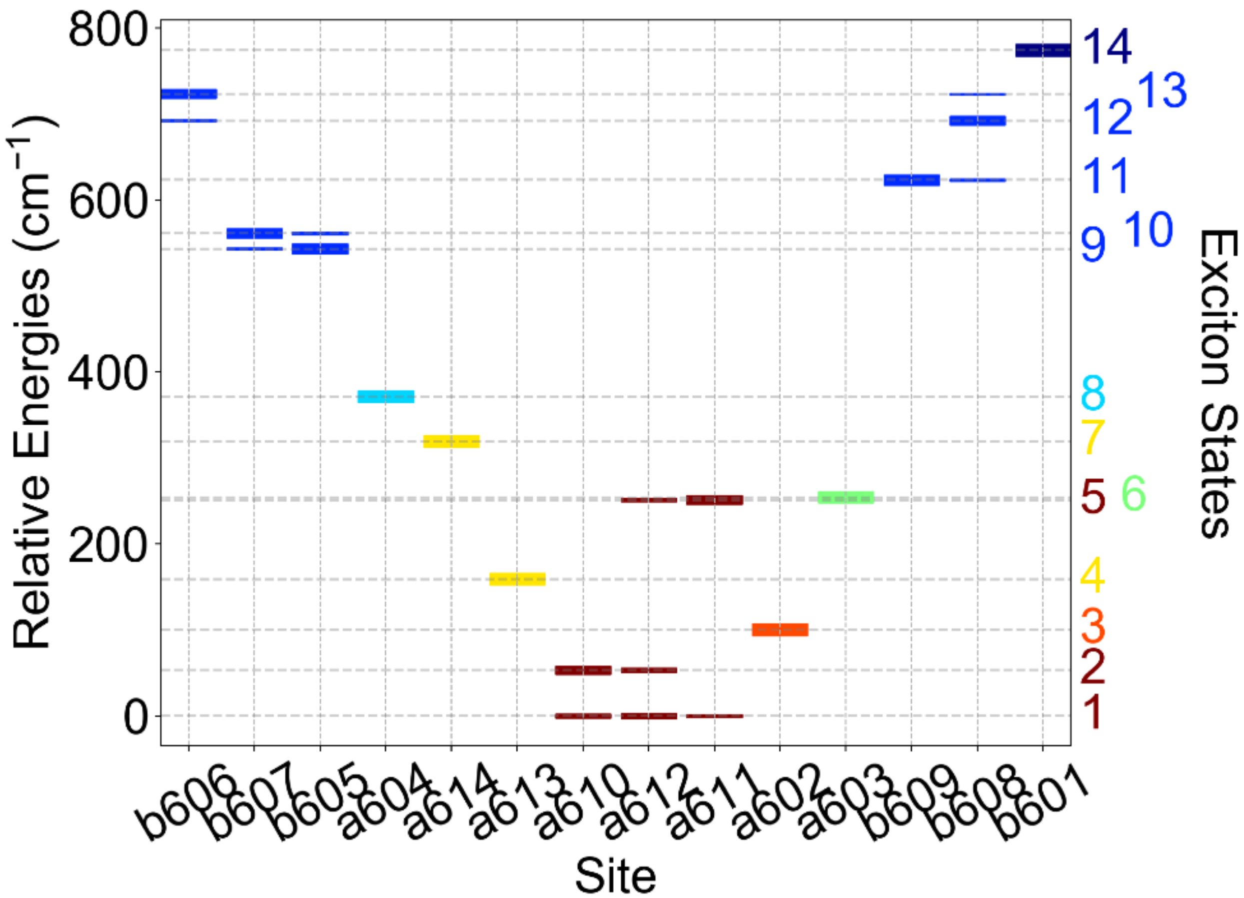


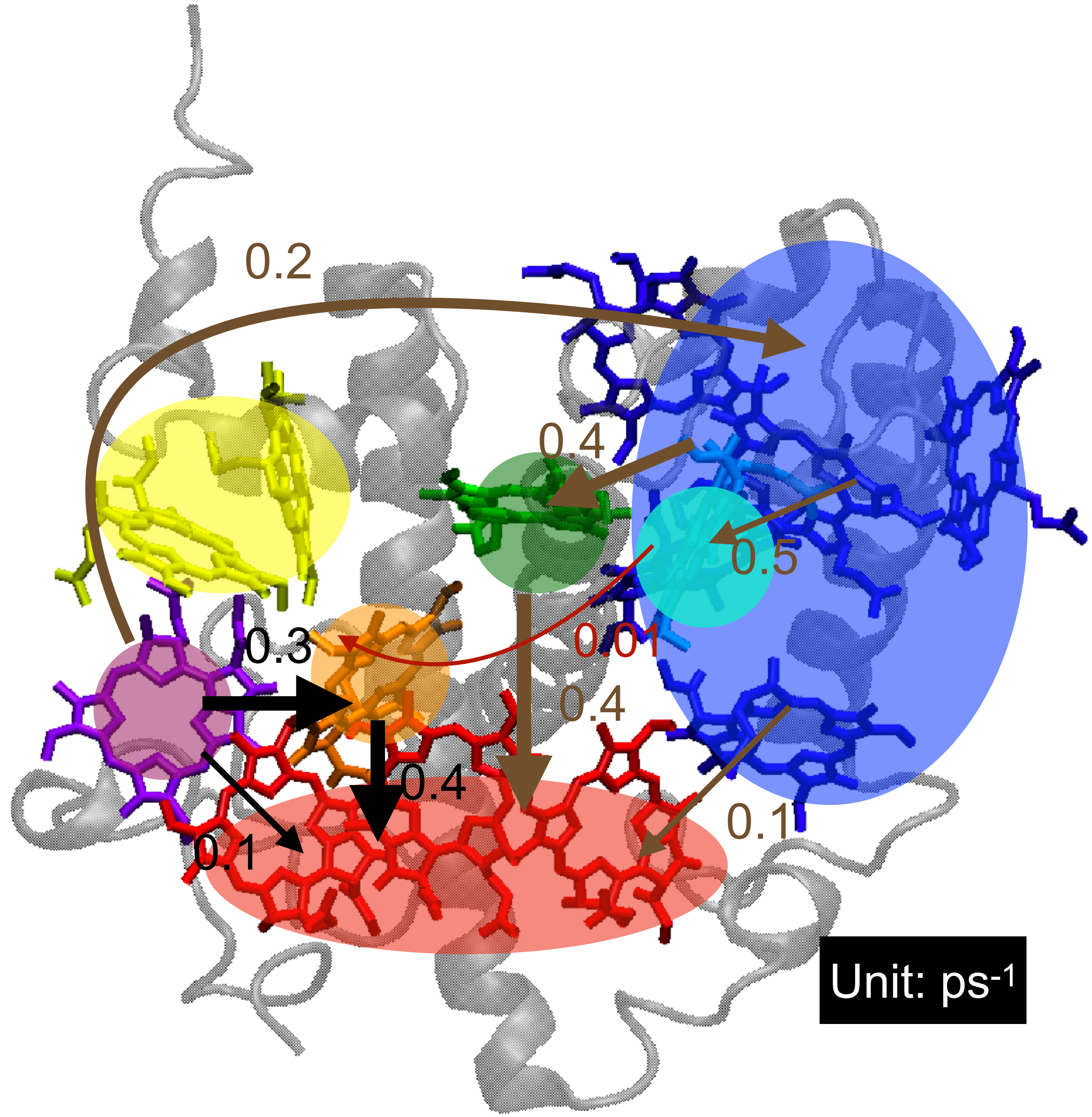
7-cluster BUC CGM

FFA pathway decomposition:

From 14 to 1:
44%: 14 -> 3 -> 1,2,5
15%: 14 -> 9,10,11,12,13 -> 6 -> 1,2,5
14%: 14 -> 1,2,5
11%: 14 -> 9,10,11,12,13 -> 1,2,5

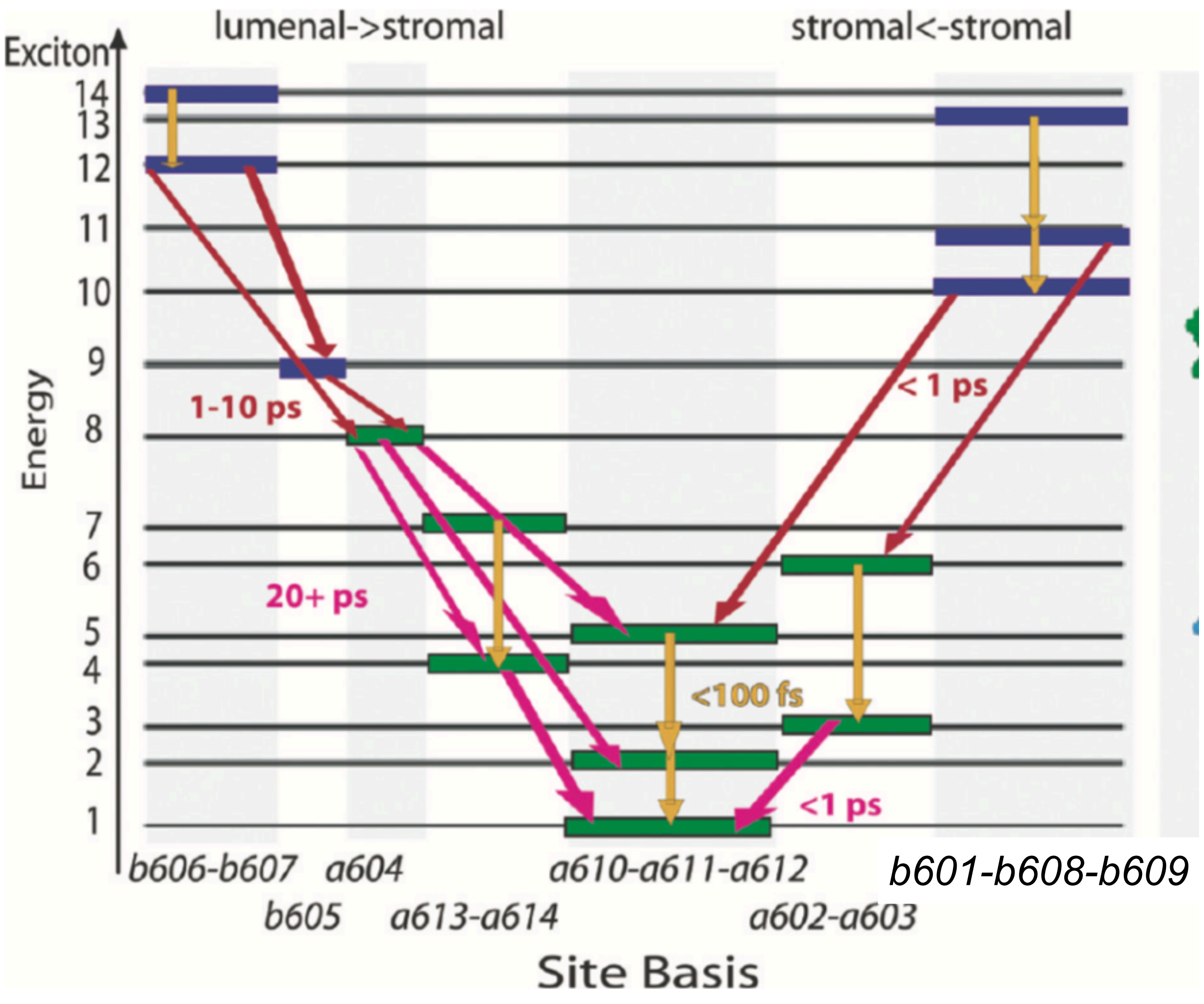
From 13 to 1:
67%: 9,10,11,12,13 -> 6 -> 1,2,5
16%: 9,10,11,12,13 -> 1,2,5

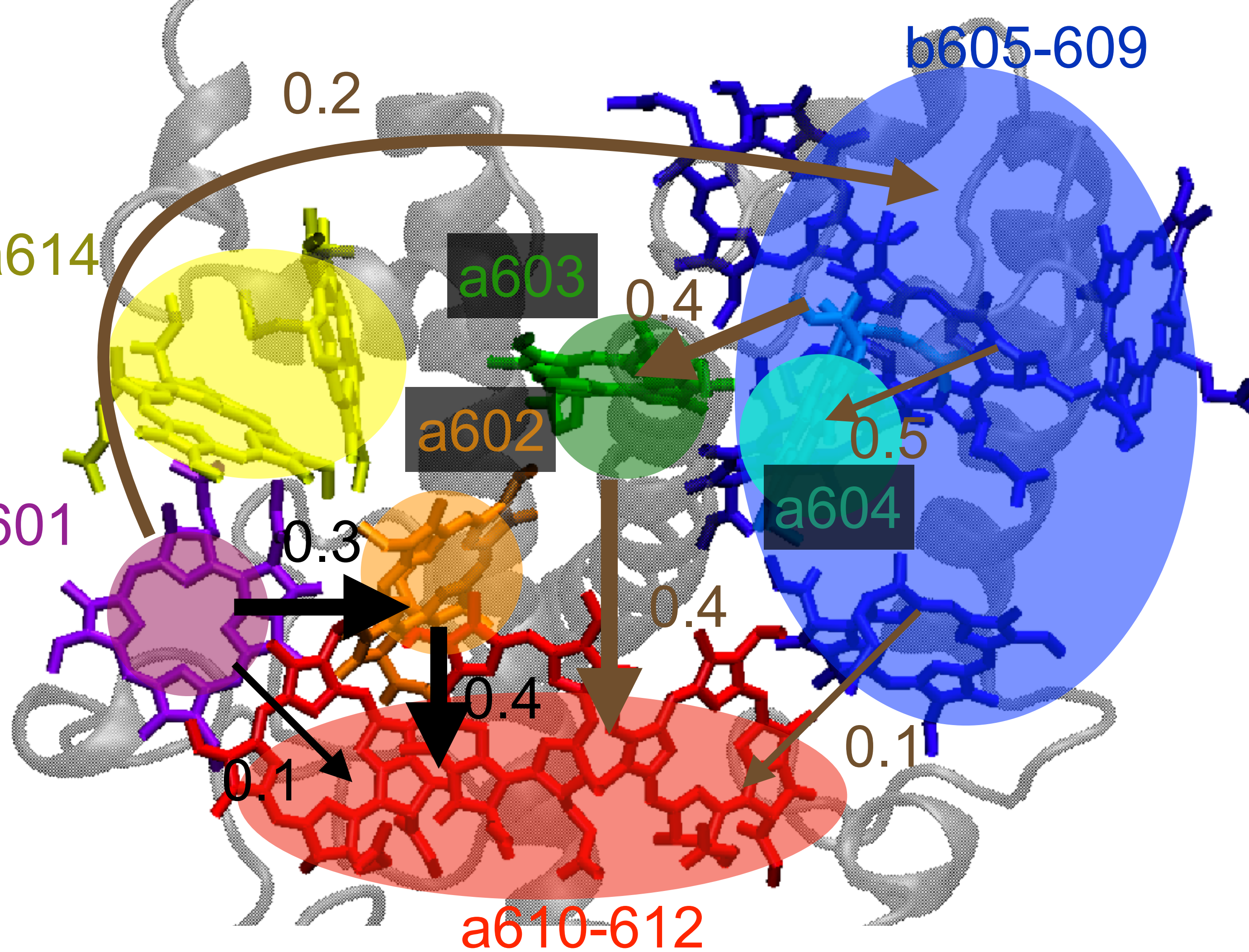




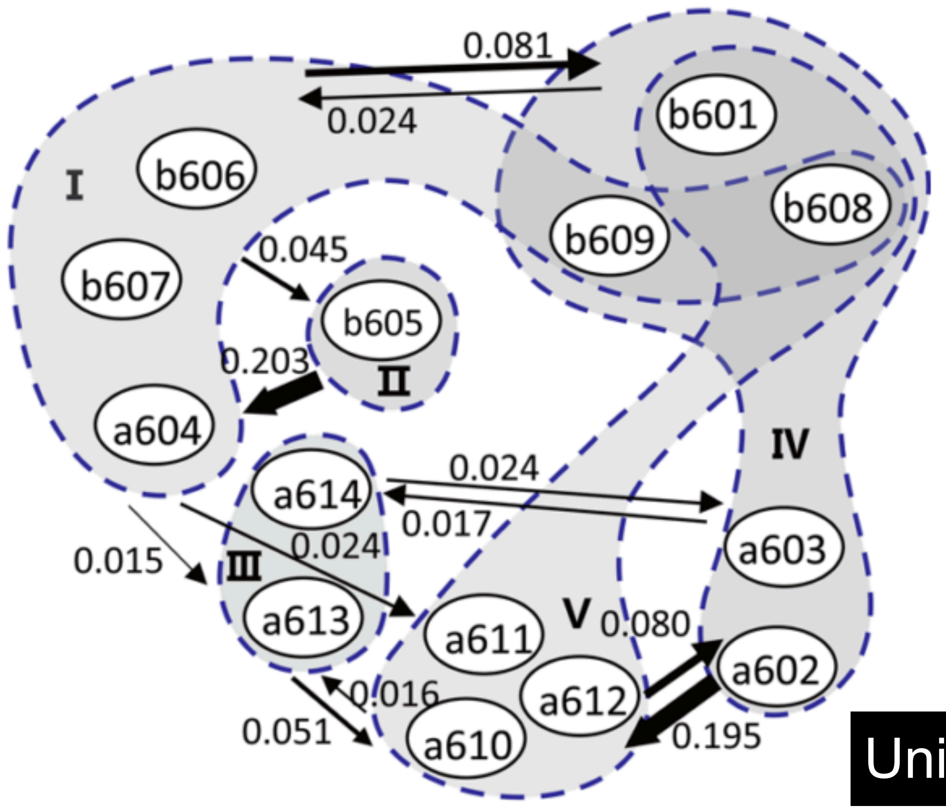
Pathways Comparison

Schlau-Cohen, G. S. et al *JPC B* **2009**, *113*, 15352





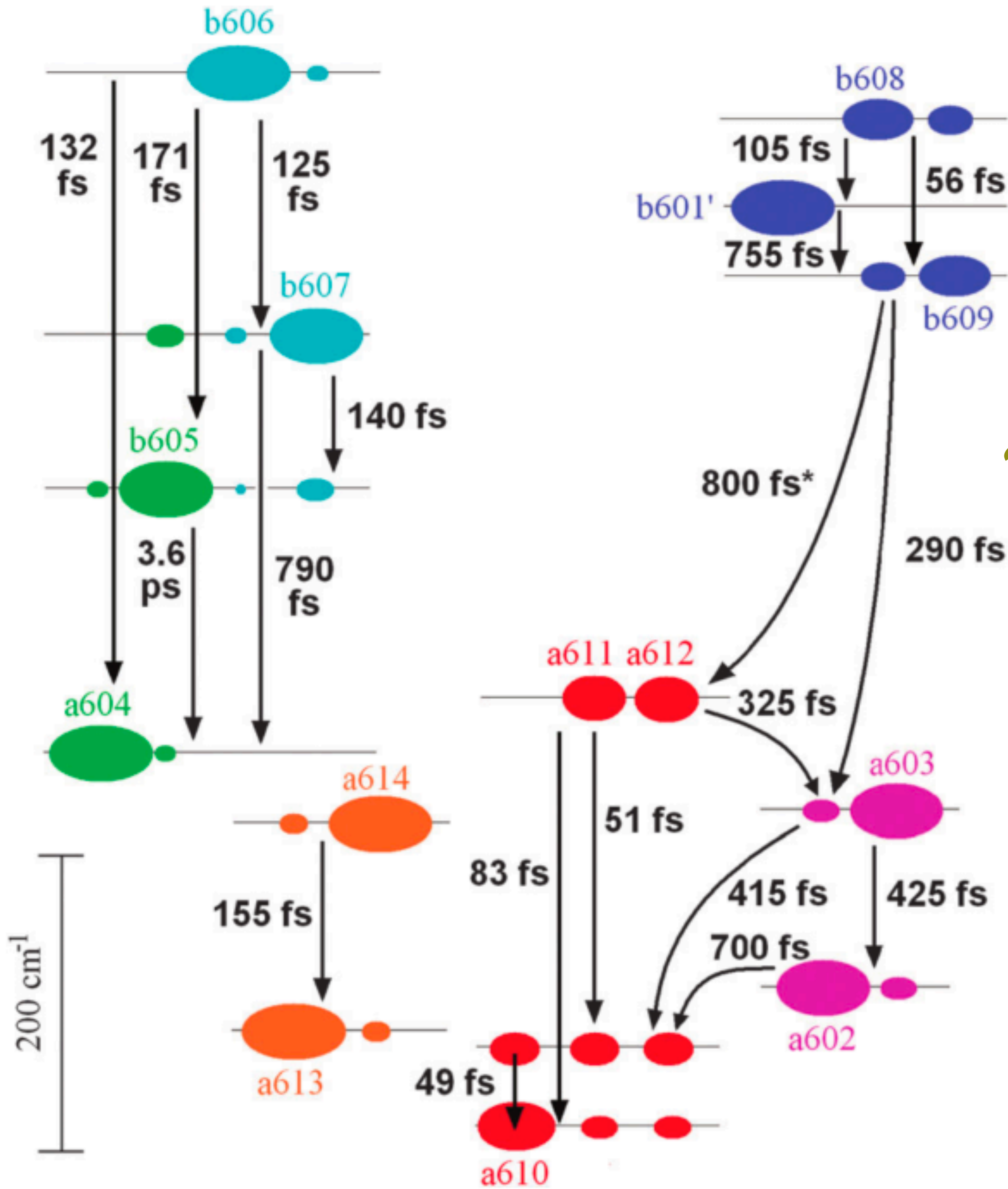
Wu, J. et al *JPCL* **2015**, *6*, 1240

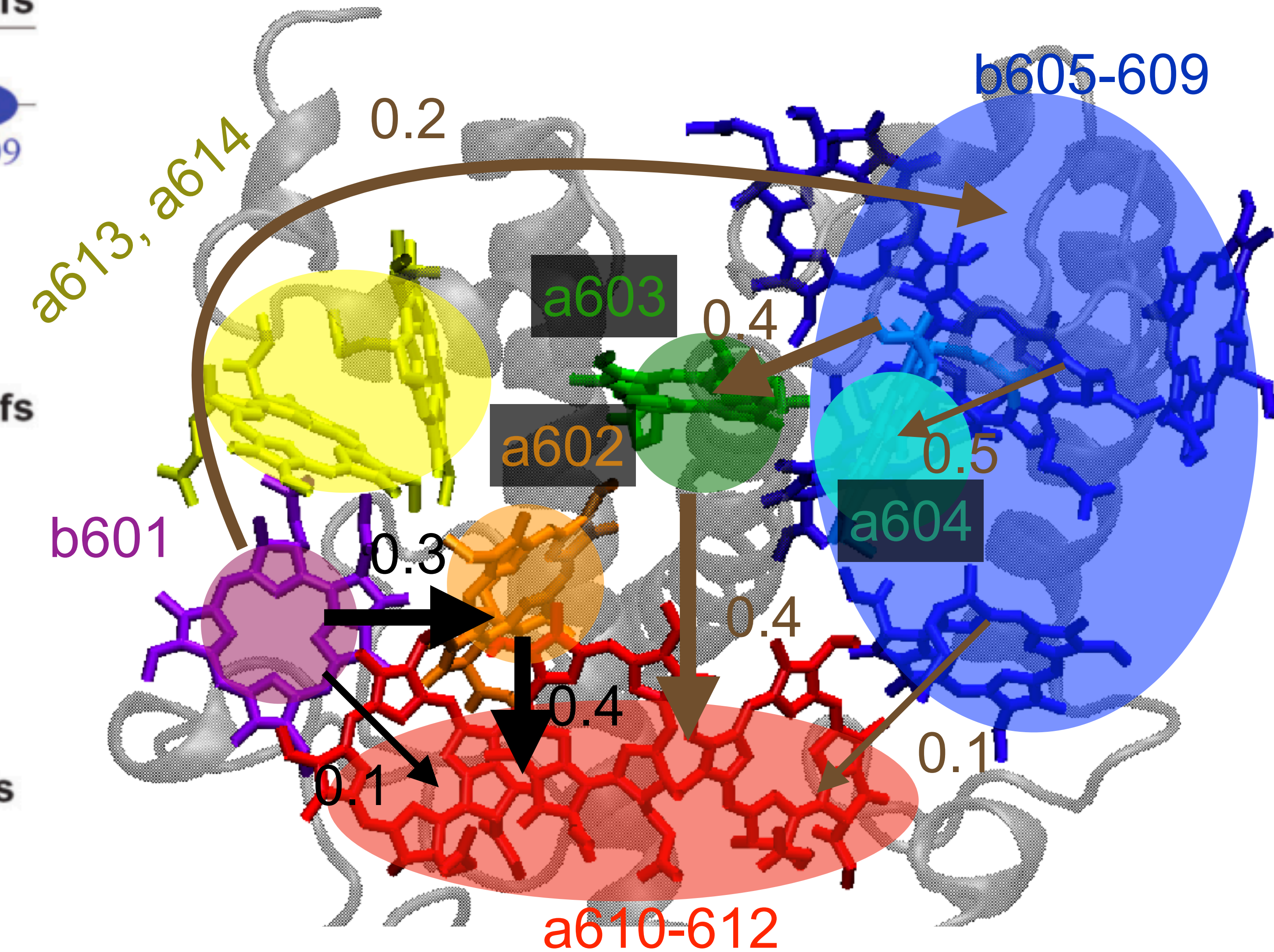


Unit: ps^{-1}

Pathways Comparison

Wells, K. L. et al *PCCP* **2014**, *16*, 11640





Summary

- The systematic coarse-graining approach utilizing the directed minimum-cut tree provides an effective tool to elucidate the dynamics of energy-transfer networks in light harvesting systems.
- We use the above-mentioned method to build up the coarse-grained models of the FMO complex and the LHCII monomer, and the energy pathways in the models are revealed by the Ford-Fulkerson algorithm.

Thanks for Your Listening