NSF Summer School UIUC 2003
Molecular Machines of the Living Cell: Photosynthetic Unit from Light Absorption to ATP Synthesis

Melih Sener  Thorsten Ritz  Ioan Kosztin

Beckman Institute

Ana Damjanovic  Theoretical Biophysics Group
(also Sanghyun Park, Deyu Lu, and Ulrich Kleinekathoefer)
Research Opportunities in the Teraflop Era

Towards Larger Molecules

BPTI
3K atoms

Estrogen Receptor
36K atoms (1996)

ATP Synthase
327K atoms (2001)

- Studying protein-protein and protein-nucleic acid recognition and assembly.

- Investigating integral functional units (membrane proteins, signal transduction, motors, bioenergetic apparatus).

- Bridging the gap between computationally feasible and functionally relevant time scales.

- Combining classical molecular dynamics simulations with quantum chemical forces.

- Describing integral cell functions.
Molecular Machines of the Living Cell

Study of integral cell functions:

gene storage, regulation, and expression; protein synthesis and degradation; energy conversion and storage; cell motion; cell signaling; metabolic pathways; …
Habitats of Photosynthetic Life Forms
Photosynthetic Apparatus of Purple Bacteria

RC - Photosynthetic Reaction Center
LH – Light Harvesting Complex
Structure of RC+LH-I+Cyt System

Focussing on the Structure of RC + LH-I
Focussing on the Structure of RC+LH-I+Cyt

System of Water - Lipids - Protein
Focussing on the Structure of RC+LH-I+Cyt

Lipids only
Focussing on the Structure of RC+LH-I+Cyt

Lipids and Proteins
Focussing on the Structure of RC+LH-I+Cyt

Proteins only
Focussing on the Structure of RC+LH-I+Cyt

Proteins and Chromophores
Focussing on the Structure of RC+LH-I+Cyt

Chromophores only
Focussing on the Structure of RC+LH-I+Cyt

Chromophores only
Electron Transfer Chain in RC + Cyt c Complex
Role of the Protein Matrix on Electron Transfer
Role of Thermal Disorder on Electron Transfer in the Photosynthetic Reaction Center

We wanted to describe how electron transfer is coupled to the thermal motion of the surrounding protein.
Electron Transfer Process Coupled to the Protein Matrix

We assumed that the electron transfer

\[ Q_A^- Q_B^- \rightarrow Q_A^- Q_B^+ \]

is coupled to an ensemble of oscillators representing the protein matrix.

Hamiltonian

\[
\hat{H}_{q_0}^{(s)} = \begin{pmatrix}
\hat{H}_r^{(s)} & v \\
v & \hat{H}_p^{(s)} + E
\end{pmatrix}
\]

Protein matrix is a bath of oscillators linearly coupled to the electron transfer according to

\[
\hat{H}_r = \sum_j \left( \frac{\hat{p}_j^2}{2M_j} + \frac{1}{2} M_j \omega_j^2 q_j^2 \right)
\]

\[
\hat{H}_p = \sum_j \left( \frac{\hat{p}_j^2}{2M_j} + \frac{1}{2} M_j \omega_j^2 \left( q_j - \frac{c_j}{M_j \omega_j^2} \right)^2 \right)
\]


**Electron Transfer Process** Coupled to the Protein Matrix

Rate for an ensemble of oscillators (spin boson model, Legett et al)

\[
k_{qb}(R \rightarrow P) = \frac{v^2}{\hbar^2} \int_{-\infty}^{+\infty} dt \ e^{itE/\hbar} e^{iQ(t)/\pi\hbar} e^{-Q_2(t)/\pi\hbar}
\]

Relaxation rate

\[
k_{\text{rel}} = \frac{2v^2}{\hbar^2} \int_{0}^{+\infty} dt \ \cos\left(\frac{tE}{\hbar}\right) \cos\left(\frac{Q_1(t)}{\pi\hbar}\right) e^{-Q_2(t)/\pi\hbar}
\]

\[
Q_1(t) = \frac{\pi}{2} \sum_j \frac{c_j^2}{\hbar\omega_j^3} \sin\omega_j t
\]

\[
Q_2(t) = \frac{\pi}{2} \sum_j \frac{c_j^2}{\hbar\omega_j^3} \coth\frac{\hbar\omega_j}{2kT} \left[ 1 - \cos(\omega_j t) \right]
\]

But we didn’t know all the coupling constants \(c_j\)? All we needed to know was \(J\)

\[
J(\omega) = \frac{\pi}{2} \sum_j \frac{c_j^2}{\omega_j} \delta(\omega - \omega_j)
\]

\[
Q_1(t) = \int_{0}^{\infty} d\omega \omega^{-2} J(\omega) \sin\omega t
\]

\[
Q_2(t) = \frac{\pi}{2} \int_{0}^{\infty} d\omega \omega^{-2} J(\omega) \coth\frac{\hbar\omega}{2kT} (1 - \cos\omega t)
\]
Electron Transfer Process Coupled to the Protein Matrix

Relaxation rate

\[
\kappa_{\text{rel}} = \frac{2v^2}{\hbar^2} \int_0^{+\infty} dt \cos\left(\frac{tE}{\hbar}\right) \cos\left(\frac{Q_1(t)}{\pi \hbar}\right) e^{-Q_2(t)/\pi \hbar}
\]

\[
Q_1(t) = \int_0^\infty d\omega \omega^{-2} J(\omega) \sin \omega t
\]

\[
Q_2(t) = \frac{\pi}{2} \int_0^\infty d\omega \omega^{-2} J(\omega) \coth \frac{\hbar \omega}{2kT} (1 - \cos \omega t)
\]

\[
J(\omega) = \frac{\sigma^2}{k_B T} \int_0^{+\infty} dt \ C(t) \cos \omega t
\]

\[
C_{\varepsilon\varepsilon}(t) = \frac{\langle (\varepsilon(t) - \langle \varepsilon \rangle) (\langle \varepsilon(0) - \langle \varepsilon \rangle) \rangle}{\langle \varepsilon(0) - \langle \varepsilon \rangle \rangle^2}
\]

energy gap correlation function

\[
\sigma \quad \text{rms deviation of energy gap}
\]

\[
\epsilon(t) = \hat{H}_p - \hat{H}_r + E
\]

energy gap
from MD
1989

1994
Temperature Dependence of Electron Transfer Rate


Electron Transfer

Coupling protein motion to electron transfer via MD

• Cytochrome $c_2$ from purple bacterium *Rhodobacter sphaeroides*.

• Serves as electron carrier between bc1-complex and reaction center

When the gene encoding cytochrome $c_2$ is deleted from *Rb. sphaeroides*, the bacterium is unable to grow photosynthetically.
Electron Transfer

The energy gap function

\[ \mathcal{G}(t) = E_P(t) \mathcal{G} E_R(t) \]

- \( R \): reactant state (reduced)
- \( P \): product state (oxidized)

**Tutorial:**
You will do two consecutive NAMD runs.

- obtain an MD trajectory
- evaluate \( \mathcal{G}(t) \) at each frame of the first trajectory through a second NAMD run
Electron Transfer

MD simulation of the electron transfer process

- ~12000 atoms solvated system
- Already minimized and equilibrated
- You will continue from a restart file
  (so, you do not need to worry about velocity relaxation)
Electron Transfer

The energy gap function

Result from the first 500 fs
Electron Transfer

The energy gap function

You will be given a longer trajectory…
Electron Transfer

The energy gap function
Genomic Organization of the Light Harvesting Complexes

- BCHla metabolism
- Carotenoid metabolism

**Genome Elements:**
- puc
- puh
- LhaA
- Bch
- Bch
- Crt
- Bch
- puf

**Orf Distribution:**

- BA(CDE) 162a 274 162b 214 puhA
- Q(BA)LMX

**Proteins:**
- LH2 apoproteins
- PucC, D, E

**LhaA:** light-harvesting complex assembly

**Molecular Features:**
- H-subunit
- 5 ORFs
- LH1 apoproteins
- L-subunit
- M-subunit
- PufQ, PufX

**Stability:**
- 3’ -> 5’ mRNA degradation
- Half-life: 8 min
- Half-life: > 20 min
Photosynthetic apparatus of purple bacteria

Xiche Hu\textsuperscript{1}, Thorsten Ritz\textsuperscript{2}, Ana Damjanovi\'c\textsuperscript{2}, Felix Autenrieth\textsuperscript{2} and Klaus Schulten\textsuperscript{2,*}

\textsuperscript{1}Department of Chemistry, University of Toledo, Toledo, OH 43606, USA
\textsuperscript{2}Beckman Institute and Department of Physics, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

1. Introduction  2

2. Structure of the bacterial PSU  5
   2.1 Organization of the bacterial PSU  5
   2.2 The crystal structure of the RC  9
   2.3 The crystal structures of LH-II  11
   2.4 Bacteriochlorophyll pairs in LH-II and the RC  13
   2.5 Models of LH-I and the LH-I–RC complex  15
   2.6 Model for the PSU  17

3. Excitation transfer in the PSU  18
   3.1 Electronic excitations of BCHls  22