Electron Transfer in the Photosynthetic Reaction Center

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Abstract

Photosynthesis occurs via electron transfer between pigment molecules or prosthetic groups embedded in a thylakoid membrane protein complex. These pigments form the "conductive pathway" for electron flow and the surrounding protein serves as a"shaping insulator". Electron transfer through the protein proceeds via quantum tunneling into succesively lower potential wells represented by the pigments. The structure of the reaction complex in the anoxygenic purple bacteria namely *Rhodopseudomonas viridis*, are surely the best understood of all reaction center complexes and will serve as a suitable model system for computation of transmission probabilities and rates of electron transfer.

1 Introduction

Photosynthesis is the process in which electromagnetic energy (light) is converted into chemical energy. Light reactions take place in the thylakoid transmembrane protein complexes; photosystems I and II (PSI and PSII). PSI is the only photosystem present in green and purple bacteria whereas cyanobacteria, algae, and the higher plants have both PSI and PSII. PSI reduces $NADP^+$ to NADPH which plays a role in ATP synthesis, and PSII forms O_2 necessary for cellular respiration from H_2O. [1] The reaction center protein complex of the purple bacterium *Rhodopseudomonas viridis* consists of 4 subunits. (Fig. 1a) The embedded pigments in Fig. 1 can be seen as wire models. In this work only the pigments of the transmembrane subunits L and M will be considered in the electron transport. The pigments contained in subunits L and M consist of a "special pair" of chlorophylls ($BChl_2$), accessory chlorophylls ($BChl_A$ and $BChl_B$), the pheophytins (BPh_A and BPh_B), and the quinones (Q_A and Q_B). [3] (Fig. 1b) The structure of photosynthetic reaction center and its cofactors has been determined by X-ray crystallography to high resolution (<2.5Å). [8]

The reaction begins through excitation of the special pair of chlorophylls either by photon absorption or indirectly through excitation transfer from the light harvesting complex adjacent to the reaction center. The electron then proceeds through the accessory chlorophyll $BChl_A$, the pheophytin BPh_A, and both quinones (Q_A then Q_B).

Chlorophylls, pheophytins, quinones, and other pigments contain π-electron bonds in a partial double structure. This provides a potential well where electrons are delocalized.[3] The transfer from one pigment to the next is achieved by quantum tunneling. The electron wavefunction actually extends beyond the potential well in which the electron resides. Because the successive potential wells created by the pigments have lower potential energies, the electron, with sufficient time tunnels to the adjacent pigment. This proceeds until the electron reaches the quinone Q_B. This process completes the half-cycle of electron transport through the L subunit. The next half-cycle consists of another electron transport event through the L subunit making Q_B doubly charged.

Interestingly the rate of electron transfer along the A pathway through the L subunit is a factor of 20 larger than that of the B pathway through the M subunit ($BChl_B \rightarrow BPh_B \rightarrow Q_B$). This is

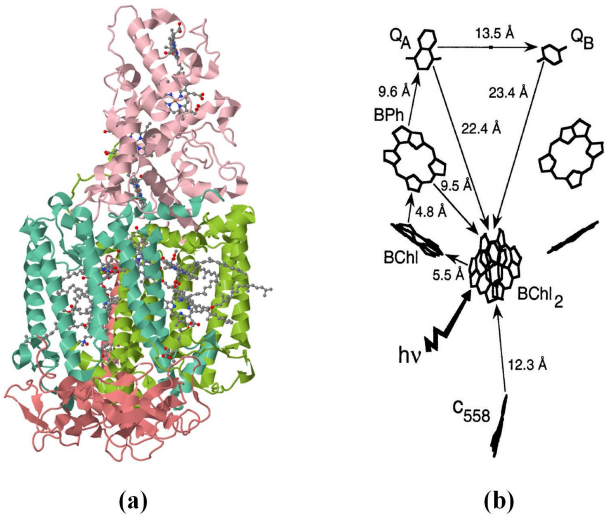

Figure 1: (a) Photosynthetic reaction center from the purple bacterium *Rhodopseudomonas viridis*. Cytochrome subunit (light pink, top), M subunit (teal, left), L subunit (green, right), H subunit (dark pink, bottom). Figure produced from the Protein Data Bank file 1PRC using Jmol molecular viewer. (b) Cofactor arrangement of the electron transfer pathway.[4] (Orientation of cofactors is a 180°rotation with respect to (a))

confirmed by picosecond absorbance transient difference spectroscopy.[3] [5]. The reason for this may lie in the very slight asymmetry between the two pathways.[8]

The process of electron transfer is a type of reduction-oxidation reaction,

$$D + A \longrightarrow D^+ + A^- \tag{1}$$

in which a donor species (D) is oxidized (D $\rightarrow$ D^+) and donates and electron to the acceptor molecule (A) which is reduced (A $\rightarrow$ A^-). In the photosynthetic reaction center the donor and acceptor molecules are the cofactor units ($BChl_2$, BChl, BPh, Q_A, and Q_B) embedded in the protein complex. The following redox reactions investigated in this work are $BChl_2{}^*$ $\rightarrow$ BChl, $BChl^-$ $\rightarrow$ BPh, BPh^- $\rightarrow$ Q_A, and Q_A $\rightarrow$ Q_B.

2 Approach

2.1 Transmission Probability

As a first attempt to understand the nature of biological electron transfer through the photosynthetic reaction center elementary one-dimensional quantum mechanics can be used to determine the probability an incident electron will be transmitted. Utilizing transfer matrices the probability that an electron with a certain energy will tunnel through a potential barrier is calculated. Given a piecewise potential barrier the asymptotic wavefunctions in the left-hand and right-hand regions are:

$$\psi_L = A_L e^{ik_L x} + B_L e^{-ik_L x}$$

$$\psi_R = A_R e^{ik_R x} + B_R e^{-ik_R x}$$

Here A_L and B_R are the incident wavefunction amplitudes from the left and right respectively and A_R amd B_L are the transmitted wavefunction amplitudes from the right and left respectively with $k_{R,L} = \sqrt{2m(E - V_{R,L})/\hbar^2}$. The transmition probability is then calculated in the following way,

$$T = \frac{k_R}{k_L}\left|\frac{A_R}{A_L}\right|^2 = \left|\frac{1}{t_{11}}\right|^2 \tag{2}$$

here t_{11} is the transfer matrix element. The transfer matrix relates the amplitudes for the wavefunction on the left and right side of the potential.

$$\begin{bmatrix} A_L \\ B_L \end{bmatrix} = \mathscr{T}\begin{bmatrix} A_R \\ B_R \end{bmatrix} = \begin{bmatrix} t_{11} & t_{12} \\ t_{21} & t_{22} \end{bmatrix}\begin{bmatrix} A_R \\ B_R \end{bmatrix}$$

The transfer matrix is determined from the product of matrices for the interior portion of the potential flanked by a pair of matrices; one for each of the two asymptotic regions.

$$\mathscr{T} = \begin{bmatrix} e^{ik_L a_L} & 0 \\ 0 & e^{-ik_L a_L} \end{bmatrix}^{-1}\begin{bmatrix} 1 & 1 \\ ik_L & -ik_L \end{bmatrix}^{-1}\prod_{j=1}^{N} M(\phi_j;\delta_j)\begin{bmatrix} 1 & 1 \\ ik_R & -ik_R \end{bmatrix}\begin{bmatrix} e^{ik_R a_R} & 0 \\ 0 & e^{-ik_R a_R} \end{bmatrix}$$

For E < V the M matrices have the following form,

$$M(\phi_j;\delta_j) = \begin{bmatrix} \cosh\kappa_j\delta_j & \kappa_j^{-1}\sinh\kappa_j\delta_j \\ -\kappa_j\sinh\kappa_j\delta_j & \cosh\kappa_j\delta_j \end{bmatrix}$$

with $\kappa_j = \sqrt{2m(\phi_j - E)/\hbar^2}$. Using this approach along with the known potential barrier heights (ϕ) [7] and cofactor donor-acceptor distances (δ)[4], the transmission probability can be obtained. (Fig. 2)

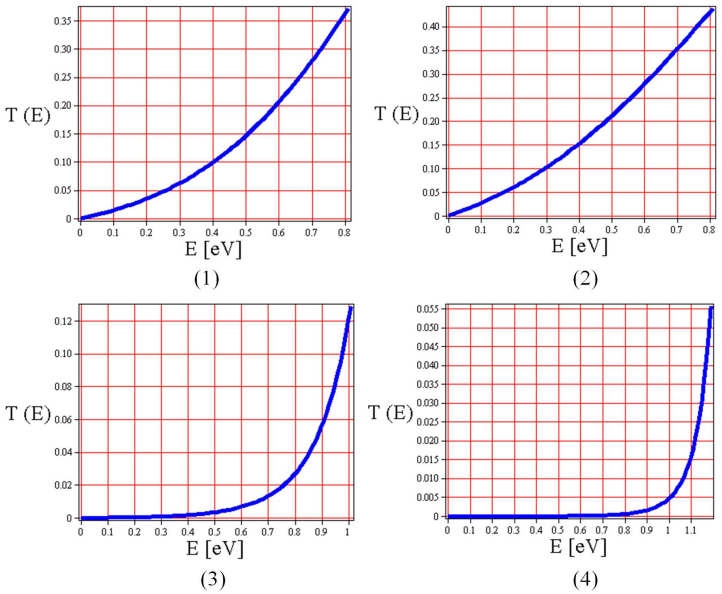

Figure 2: Transmission probabilities for electron transfer between photosynthetic pigments for E < ϕ. (1) $BChl_2^*$ → BChl, ϕ = 0.82 eV, δ = 5.5 Å. (2) $BChl^-$ → BPh, ϕ = 0.82 eV, δ = 4.8 Å. (3) BPh^- → Q_A, ϕ = 1.02 eV, δ = 9.6 Å. (4) Q_A^- → Q_B, ϕ = 1.20, δ = 13.5 Å.

2.2 Electron Transfer Rate

Of particular interest is the rate in which the electron tunneling occurs from one pigment molecule to the next. The Fermi golden rule which arises out of quantum mechanical perturbation theory describes the first-order rate constant for electron transfer processes. [5] [9]

$$k_{et} = \frac{2\pi}{\hbar}|H_{AB}|^2 FC \tag{3}$$

The follwing subsections will attempt to construct the parameters $|H_{AB}|^2$ and FC comprising eq. (3).

2.2.1 Wavefunctions

In eq. (3) H_{AB} is the electronic matrix element describing the electronic coupling of the reactant electronic state with that of the products'.

$$H_{AB}^2 = |\langle \Psi_i | \tilde{V} | \Psi_f \rangle|^2 \tag{4}$$

In eq. (4) Ψ_i and Ψ_f are the wavefunctions of the initial and final states respectively (this includes both donor and acceptor) and $\tilde{V}$ is the perturbation energy of the electron of the donor by the acceptor. The approximate wave function of the electron before and after transfer is described by the atomic orbitals $\psi_{el,i}$:

$$\Psi_{el} = \sum_i c_i \psi_{el,i} \tag{5}$$

At small distances of the electron from the nucleus i, $\psi_{el,i}$ can be represented by a Slater function (for $r_i < r_\pi$, r_π is the van der Waals radius of a π-electron),

$$\psi_{el,i} = N_{S,i}\left(\frac{r_i}{a_0}\right)\exp\left[\frac{-Z_{eff,i}r_i}{2a_0}\right]\frac{z_i}{r_i} \tag{6}$$

where $Z_{eff,i} = 3.25$ for C, 3.90 for N, and a_0 is Bohr's radius. In order to evaluate H_{AB} the wave function at large distances is needed. At large distances the electron with energy $-\epsilon$ is effectively in the field of its counter charge e_0 in a dielectric (surrounding protein) with permittivity D. [7] Thus the electron's wave function must satisfy the Schrödinger equation for $V = -e_0/(Dr)$. The solution has the following form:

$$\psi_{el,i} = N_i\left(\frac{r_i}{a_0}\right)^{n-1} e^{-\alpha r_i}\frac{z_i}{r_i} \tag{7}$$

$$\alpha = \sqrt{2m_e\epsilon}/\hbar$$

$$n = 1/(\alpha a_0 D)$$

Continuity of the wavefunction dictates that at $r = r_\pi$,

$$N_i = N_{S,i}\left(\frac{r_\pi}{a_0}\right)^{2-n}\exp\left\{\left[\alpha - \frac{Z_{eff,i}}{2a_0}\right]r_\pi\right\} \tag{8}$$

$N_{S,i}$ is given by normalizing the wave function. It is reasonable to approximate $N_{S,i}$ (for $r < r_\pi$) by normalizing the Slater function.

$$N_{S,i} = \frac{1}{\sqrt{\pi}} \left[\frac{Z_{eff,i}}{2} \right]^{5/2} a_0^{-3/2} \tag{9}$$

The final wavefunction state is obtained accordingly. The electronic matrix element can be simplified and expressed in the following exponential relationship[6]:

$$|H_{AB}|^2 = V_0^2 e^{-\beta R} \tag{10}$$

V_0^2 is the maximum electronic coupling, β is coefficient of decay of electronic coupling, and R is the edge donor atom to edge acceptor atom distance. For protein the β value is approximately 1.4 $Å^{-1}$. [6]

2.2.2 Franck-Condon Factor

FC in eq. (3) is the Franck-Condon factor which is a sum of products of overlap integrals of the vibrational and solvational wavefunctions of the reactants with those of the products weighted by Boltzmann factors. In the high temperature limit the Franck-Condon factor reduces to,

$$FC = \frac{1}{\sqrt{4\pi\lambda kT}} \exp\left[-\frac{(-\Delta G^0 - \lambda)^2}{4\lambda kT} \right] \tag{11}$$

in which ΔG^0 is the standard state Gibbs free energy change in the reaction and λ is the reorganization energy. The reorganization energy is the energy required for all structural adjustments (in the reactants and surrounding solvent molecules) which are needed in order for electron transfer without the electron transfer process actually occuring.

There are three regimes of interest in regards to the relationship between the change in free energy of the reactant and product states and the reorganization energy.[5] (Fig. 3)

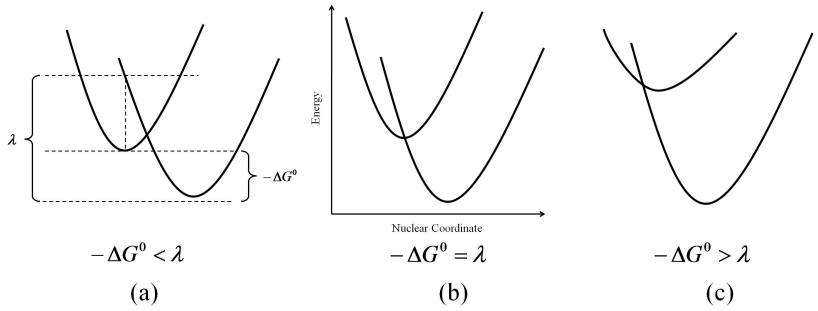

Figure 3: Potential energy diagrams for electron transfer processes according to Marcus theory. (a) $-\Delta G^0 < \lambda$. (b) $-\Delta G^0 = \lambda$. (c) $-\Delta G^0 > \lambda$. [5]

If $-\Delta G^0 < \lambda$ the process is endergonic to slightly exergonic and exhibits thermally activated behavior.[1] If the reaction becomes increasingly exergonic to the point where $-\Delta G^0 = \lambda$ then the potential energy curves for the reactants and products intersect near the minimum of the reactant potential well and the reaction is in the "activationless regime". At this point the Franck-Condon factor is at a maximum and the reaction as a result is very fast. For extremely exergonic reactions with $-\Delta G^0 > \lambda$ the system is in the "Marcus inverted" regime and the reaction rate is decreased.

[1] Def. Endergonic: system absorbs energy in the form of work. Exergonic: energy is released in the form of work.

3 Results

Using the formulation of equations (10) and (11) the overall rate equation (eq. 3) can be rewritten in the following form:

$$k_{et} = \frac{2\pi}{\hbar} V_0^2 e^{-\beta R} \frac{1}{\sqrt{4\pi\lambda kT}} \exp\left[-\frac{(-\Delta G^0 - \lambda)^2}{4\lambda kT}\right] \tag{12}$$

In the $-\Delta G^0 = \lambda$ regime the optimized rates can be plotted as a function of the donor-acceptor edge-to-edge distance.

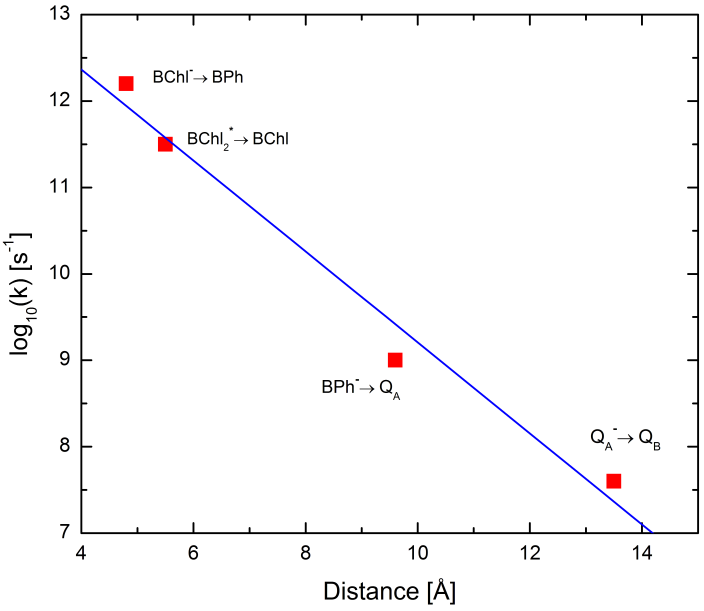

Figure 4: Free energy optimized rate versus edge-to-edge distance between donor and acceptor for electron transfer [6]

The kinetics of each individual electron transfer reaction has been experimentally measured by time-resolved optical spectroscopy. [8] (Fig. 5) The reactions $BChl_2{}^*$ → BChl and $BChl^-$ → BPh are commonly combined due to the extremely fast transfer time of approximately 4 ps. Next the reaction BPh^- → Q_A occurs in about 230 ps. Followed by the very slow transfer time of about 100 μs for Q_A → Q_B.

It is interesting to note that charge recombination is possible between the special pair of $BChl_2$ cofactors throughout the entire reaction. The transfer process is stabilized against charge recombination for progressivley longer periods. [8] The ratios of forward transfer rates to charge recombination rates are approximately 10^2 - 10^3, resulting in a high quantum yield. [8]

4 Discussion

According to the theory of Marcus, electron trasnfer is heavily dependent on three factors; the overlap of the electron wavefunctions (directly dependent on edge-to-edge donor-acceptor distance), the difference in Gibbs free energy between initial and final states, and the reorganization energy. [9] The theory

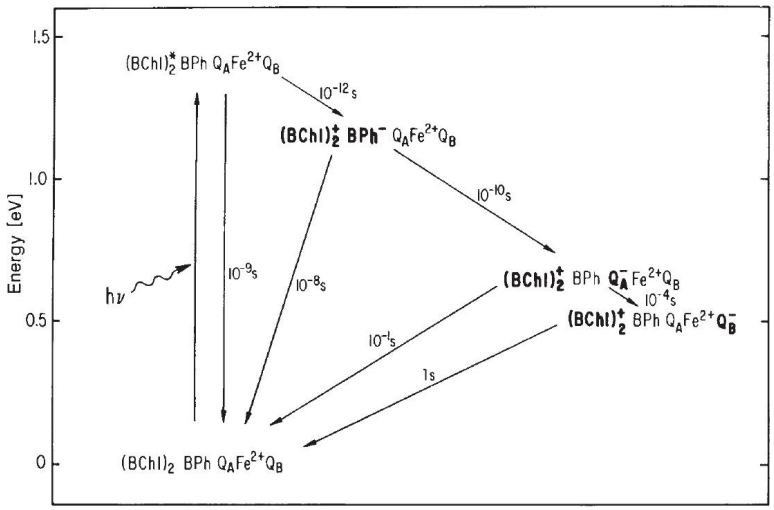

Figure 5: Electron transfer kinetics for the vairous donor-acceptor complexes in the bacteria *Rhodopseudomonas viridis* at room temperature. [8]

predicts that the transfer rate will be optimal when the reorganization energy is equal to the change in free energy ($\lambda = -\Delta G^0$). Most importantly the distance spacing parameter provides a 10^{12}-fold range of rates (including charge recombination) and can be directly implicated in the promotion of physiologically productive electron transfer and repression of non-productive transfer events. [6] It is believed that evolution has shaped the forms of photosynthetic reaction centers which build upon natural parameters such as β and modulated ΔG^0, λ, and most importantly R (distance) through natural selection to obtain optimal transfer rates.

Using electronic spectroscopy measurements made on femtosecond time scales, evidence has surfaced indicating that electronic quantum coherence plays an important role in photosynthetic energy transfer processes. [10] This evidence helps to explain the extreme efficiency with which energy transfer occurs in the photosynthetic reaction center because it enables the system to choose the most efficient path by sampling all possible potential energy pathways. It has been suggested in the past that energy transfer might involve quantum oscillations but was dismissed by the scientific community because the electronic coherences responsible were assumed to be rapidly destroyed. [11] In this way the "classical" (Markovian) electron transfer theories applied to photosynthetic reaction centers need to be re-evaluated and perhaps modified to account for coherent energy transfer dynamics.

References

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A Transmission Probability Code

```
V:=Array([0,1.20,0]);
L:=Array([0,13.5,0]);

Emax:=V[2];
dE:=0.01;
Ep:=Array(1..Emax/dE);
Tp:=Array(1..Emax/dE);
ArrayNumElems(Ep);

j:=1:

for E from 0 to Emax by dE do

for i from 1 to ArrayNumElems(V) do

if E > V[i] then
k:=0.5125*sqrt(E-V[i]);
M:=Matrix([[cos(k*L[i]),-(sin(k*L[i]))/k],[k*sin(k*L[i]),cos(k*L[i])]]);
end if;

if E = V[i] then
M:=Matrix([[1,-L[i]],[0,1]]);
end if;

if E < V[i] then
kappa:=0.5125*sqrt(V[i]-E);
M:=Matrix([[cosh(kappa*L[i]),-(sinh(kappa*L[i]))/kappa],[-kappa*sinh(kappa*L[i]), cosh(kappa*L[i
end if;
```

```
if i = 1 then
Mp:=M;
end if;

if i > 1 then
Mfin:=Mp.M;
Mp:=Mfin;
end if;

k0:=0.5125*sqrt(E):

T:=4 / ( ((Mfin[1,1]+Mfin[2,2])^2) + ((k0*Mfin[1,2]-Mfin[2,1]/k0)^2) ):

end do:

Ep[j]:=E:
Tp[j]:=T:

j:=j+1:

end do:
```