Dynamical Theory of Primary Processes of Charge Separation in the Photosynthetic Reaction Center

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Abstract. A dynamical theory has been developed for primary separation of charges in the course of photosynthesis. The theory deals with both hopping and superexchange transfer mechanisms. Dynamics of electron transfer from dimeric bacteriochlorophyll to quinone has been calculated. The results obtained agree with experimental data and provide a unified explanation of both the hierarchy of the transfer time in the photosynthetic reaction center and the phenomenon of coherent oscillations accompanying the transfer process.

Key words: charge oscillation, hopping, quinone, Schrödinger equation, superexchange

1. Introduction

Photosynthesis is a process in which light energy converts into energy necessary for functioning of living organisms. This process involves reactions in which light energy absorbed by pigments of a photosynthesizing organism changes directly into the energy of chemical bonds and photosynthetic products. An important problem is to study mechanisms of the initial stages of photosynthesis [1–3].

Photosynthetic light reactions begin with absorption of a light quantum at the edge of the reaction center occurring near the membrane internal surface. An electron excited due to light absorption transfers photon energy to the opposite edge of the reaction center localized near the membrane external surface. As a result of this transfer, charges separate: electrons accumulate near the membrane external surface, and the internal surface assumes positive charge.

The main form of accumulating light energy is an electron current, which is not merely a set of individual oxidation-reduction reactions but a directional chain of electron transport through intermediates localized in photosynthetic membranes. Accumulation of energy due to charge separation in the photoreaction center occurs at a high level of efficiency unattainable in modern technical devices.

When a reaction center absorbs a light quantum, its molecular structure undergoes some changes as a result of which an electron is transported across the

membrane over a distance of up to 50 Å. One can keep track of these changes by studying the absorption spectrum of a photoreaction center. This study enables one to reveal a “chemical pathway” of an electron from one side of the membrane to the other. Another method of tracing the electron pathway involves the use of electron paramagnetic resonance.

Spectroscopic methods have enabled one to reveal sequences and time characteristics of electron transfer reactions occurring in the photosynthetic reaction center due to light absorption. The process of photosynthesis begins with absorption of a light quantum by chlorophyll molecules which are referred to as a special pair and occur at the edge of the reaction center residing near the membrane internal surface. Then an excited electron quickly travels to pheophytin, bypassing monomeric chlorophyll. The main peculiarity of the primary processes is in the fact that the initial stages of electron transfer, i.e. detachment of an electron from chlorophyll and reduction of a primary acceptor, proceed in reaction centers (RC) very quickly, during a few picoseconds ($\sim 3 \times 10^{-12}$ s). As a result, a special pair assumes a positive charge. On leaving pheophytin, an electron travels to quinone residing near the membrane external surface and then goes to another quinone molecule occurring on a symmetrical branch of the reaction center. The latter reaction proceeds very slowly. Its rate is nearly 10^8 times less than the rate of electron transfer to pheophytin. Thereon the primary stage of charge separation is completed. Efficiency of primary processes in reaction centers is very high. It has been determined experimentally and appeared to be close to unity – nearly 100%.

Though the general scheme of the reaction center performance is clear, some important details require more close consideration. In particular, down to recent times, considerable study has been given to elucidating the role of monomeric chlorophyll: whether it is a chemical intermediate in the course of charge transfer or just a mediator of the transfer [4–16]. In this context, development of a theory which could describe dynamics of primary charge separation in a photoreaction center assumes special importance.

Such a theory has been built in [17] with an emphasis on the dynamics of electron transfer during the first 3 ps when an electron passes on from dimeric bacteriochlorophyll to pheophytin. This paper is devoted to modeling the dynamics of electron transfer during 200 ps when an electron travels to quinone. These calculations are necessary, first of all, to describe completely the primary chain of electron transfer in the reaction center (RC).

Subsequent stages of electron transfer require participation of mobile charge carriers and after the second quinone go beyond the reaction center. As was shown in [18], these subsequent stages can efficiently be described with the use of imitation modeling. From an applied viewpoint, detailed information on primary photosynthetic processes is necessary for successful development of molecular genetics of photosynthesizing organisms, which would enable one to change reaction centers by way of genetic manipulations and assess how quickly and efficiently the new proteins realize the electron transfer. The importance of these investigations is also

concerned with the fact that the photosynthetic reaction center is presently considered as a potential element in prospective nanotechnology devices which have no equal in efficiency.

2. Primary Processes of Charge Separation in a Photosynthetic Reaction Center

A primary process in a photosynthetic reaction center is a transition of an electron from its primary donor – dimeric bacteriochlorophyll P – to quinone Q_A . In the modern view [1–3], monomeric bacteriochlorophyll B and bacteriopheophytin H also take part in the transfer (Figure 1). Super-fast initial stages of the transfer were studied in detail in a number of RCs where the donor of an electron was a light-excited dimeric bacteriochlorophyll P^* with a lifetime of the excited state of approximately $\sim 3 \times 10^{-10}$ s and the primary acceptor was bacteriopheophytin H [19–23]. The short lifetime of an excited dimeric P^* necessitates the transfer to the monomer to be two orders of magnitude faster. Otherwise there will not be a chance for RC to “catch” the photosynthetic excitation energy and it will change to heat and fluorescence.

After early measurements of the rate of such a transfer (≈ 3 ps for the transition of $P^* \rightarrow H$ and 200 ps for the transition of $H \rightarrow Q_A$ at $T = 293$ K),

Figure 1. Photosynthetic reaction center (Rhodobacter sphaeroides).

most investigations in the field centered on elucidating the role of monomeric bacteriochlorophyll B residing between dimeric P and bacteriopheophytin H. A large distance between P and H (≈ 10 Å edge to edge) and an extremely large electron transfer rate together with slow recombination have not enabled researchers to interpret the transition $P^* \rightarrow H$ as direct, i.e. without participation of an intermediate B.

Two different approaches have been discussed [21–26]. In the first one bacteriochlorophyll has been considered as a real intermediate when an electron hops from P^* to B and then to H. In the second approach B plays the role of a virtual intermediate when an electron hops from P^* directly to H. This case corresponds to a superexchange transfer mechanism (dotted line in Figure 1). According to the results of [17] both the approaches are just two limit cases of a dynamical model based on a quantum-classical description of primary processes of charge separation. Actually, a combination of the two processes takes place, determining a complicated dynamics of electron transfer between P^* , B and H. Notice also that, apart from monomeric B, some works have discussed a possible role of a water molecule occurring near dimeric bacteriochlorophyll which reduces the potential barrier induced by the dipole moment of the dimer-monomer system [27, 28].

So, despite a great number of experiments and theoretical works devoted to the problem, a detailed dynamics of such a transfer is still to be clarified. The use of differential spectroscopy (in which absorption spectra with various delays are measured) has revealed a decisive role of oscillations of atomic nuclei in the ultra-fast processes under discussion. This method has enabled one to observe activated coherent motions and oscillations in a bacterial reaction center and unambiguously related the occurrence of coherent motions with arising of a singlet excited P^* state [19–23, 29]. In [17], the arising of such oscillations was shown to be caused by energy modulation of an excited electron (making fast reversible transitions in the P^*BH system) by nuclear dynamics.

3. Mathematical Model

In the electron transfer system under consideration, the donor of an electron is a dimeric bacteriochlorophyll P^* , intermediate carriers are monomeric B and pheophytin H and the acceptor of an electron is quinone Q_A . In keeping with [17] we write the Hamiltonian of the system in the form:

$$\hat{H} = \sum_i \alpha_i |i\rangle \langle i| + \sum_{i,i'} v_{i,i'} |i\rangle \langle i'| + \sum_{i,j} \alpha'_{ij} q_{ij} |i\rangle \langle i| \quad (1)$$

where α_i determines the electron energy at the i -th site ($i = 1, 2, 3, 4$ represent P^* , B, H and Q_A , respectively), $v_{i,i'}$ are matrix elements of the transition from the i -th site to the i' -th site. The Hamiltonian (1) takes into consideration displacements $q_{i,j}$ ($j = 1, 2, \dots, n_i$) corresponding to n_i oscillatory modes at the i -th site and $\alpha'_{i,j}$ are constants for the electron coupling with the displacements $q_{i,j}$.

It is essential that the Hamiltonian $\hat{H}$ describes both the limit cases, i.e. superexchange and hopping mechanisms of the electron transfer. Central for the description of irreversible electron transfer in the RC are oscillatory modes q_{ij} . Their inclusion simulates the active role played by the protein surroundings of the molecule-carriers.

Displacements q_{ij} can be described by classical motion equations, since effective masses M_{ij} of the atomic groups representing the oscillatory modes far exceed the electron effective mass. According to [17], these motion equations have the form:

$$M_{ij}\ddot{q}_{ij} = -\gamma_{ij}\dot{q}_{ij} - K_{ij}q_{ij} - \alpha'_{i,j}|b_i|^2 \quad (2)$$

where K_{ij} are elastic constants and γ_{ij} are friction coefficients. The quantities b_i involved in (2) are amplitudes of the probabilities of an electron occurrence at the i -th site satisfying the normalizing condition $\sum |b_i|^2 = 1$. Their values at each instant of time are determined from the solution of the Schrödinger equation corresponding to Hamiltonian (1):

$$i\hbar\dot{b}_n = \alpha_n b_n + \sum_j \alpha'_{nj} q_{nj} b_n + \sum_{n'} v_{n,n'} b_{n'} \quad (3)$$

where $\hbar = \frac{h}{2\pi}$, h is Plank's constant. The system (2), (3) is self-consistent: evolution of probability amplitudes b_n is determined by site displacements q_{nj} which, in turn, depend on the probability distribution $|b_n|^2$.

4. Model Parameters

Our model contains a great many parameters, some of which were considered earlier in the three-site model. With regard to this fact we use the following parameter values.

Frequencies. For the Rhodobacter sphaeroides dimer P we take five main frequencies: $\omega_{11} = 15 \text{ cm}^{-1}$; $\omega_{12} = 92 \text{ cm}^{-1}$; $\omega_{13} = 122 \text{ cm}^{-1}$; $\omega_{14} = 153 \text{ cm}^{-1}$; $\omega_{15} = 329 \text{ cm}^{-1}$, where $\omega_{nj} = (K_{nj}/M_{nj})^{1/2}$. The values of these five frequencies coincide with those considered in [17].

For frequencies $\omega'_{nj} = \gamma_{nj}/M_{nj}$ determining damping of oscillatory modes, we put – in conformity with [17] – $\omega'_{11} = 21.2 \text{ cm}^{-1}$; $\omega'_{12} = 10.6 \text{ cm}^{-1}$; $\omega'_{13} = 13.3 \text{ cm}^{-1}$; $\omega'_{14} = 14.3 \text{ cm}^{-1}$; $\omega'_{15} = 265 \text{ cm}^{-1}$. For monomer bacteriochlorophyll B in accordance with [17] we put: $\omega_{21} = 12 \text{ cm}^{-1}$; $\omega_{22} = 30 \text{ cm}^{-1}$. The damping frequencies are $\omega'_{21} = 53.1 \text{ cm}^{-1}$; $\omega'_{22} = 53.1 \text{ cm}^{-1}$.

For pheophytin H: $\omega_{31} = 564 \text{ cm}^{-1}$; $\omega_{32} = 0.375 \text{ cm}^{-1}$; $\omega_{33} = 53.1 \text{ cm}^{-1}$. The damping frequencies are $\omega'_{31} = 595 \text{ cm}^{-1}$; $\omega'_{32} = 5.31 \text{ cm}^{-1}$; $\omega'_{33} = 531 \text{ cm}^{-1}$. So, we consider the low-frequency oscillation (which was not taken into account in [17]) ω_{32} to be highly damped: $\omega'_{32} \gg \omega_{32}$. The low-frequency oscillatory mode

ω_{32} is included to take into account oscillations of peptide groups of the protein surrounding (which lie in the frequency range of $\sim 10^{10}$ – 10^{11} s $^{-1}$ [1]). Notice that the contribution to this low-frequency made can also originate from the reorientational dynamics of dipoles (orientational Debye-type relaxation). In polar solvents the latter has a broad peak at 0.2–3 cm $^{-1}$ [30].

For quinone Q_A : $\omega_{41} = 53.1$ cm $^{-1}$, $\omega'_{41} = 53.1$ cm $^{-1}$.

Matrix elements. In conformity with [17], we take the matrix elements of the transition between dimeric P and monomeric B to be equal to the matrix elements of the transition between monomeric B and pheophytin H: $\nu_{12} = \nu_{23} = 80$ cm $^{-1}$. The matrix element of the transition between pheophytin and quinone Q_A is taken to be equal to $\nu_{34} = 345$ cm $^{-1}$.

Energy levels. For monomeric B and pheophytin H, the energies of electron states reckoned from the level of electron energy P^* are equal, as in [17], to $\nu_{22} = -106$ cm $^{-1}$, $\nu_{33} = -170$ cm $^{-1}$. For quinone Q_A we choose $\nu_{44} = -3132$ cm $^{-1}$. This value lies in the range of possible values of the free energy of electron transition from P^* to Q_A : 0.2 eV $< |\Delta G| < 0.8$ eV [12]. Notice, that in modulus, the values of ν_{22} and ν_{33} are much less than the difference between free energies $\Delta G_{22} = -0.041$ eV (which corresponds to ≈ 331 cm $^{-1}$) and $\Delta G_{33} = -0.050$ eV (which corresponds to ≈ 403 cm $^{-1}$) obtained from the analysis of experimental data [31]. This result follows from the fact that in our model the quantities ΔG_{ii} are equal to $\Delta G_{ii} = \nu_{ii} + \frac{1}{2} \sum_j \alpha'_{ij} q_{ij}$ and always exceed ν_{ii} in modulus.

Interaction constants. In [17] the dimensional values of the constants of electron interaction with oscillatory modes α'_{ij} corresponding to dimensionless values of κ_{ij} (see Appendix) have the form:

$$\begin{aligned} \tilde{\alpha}'_{11} &= 2.87 \times 10^9 \text{ eV/\AA}, \tilde{\alpha}'_{12} = 7.85 \times 10^9 \text{ eV/\AA}, \tilde{\alpha}'_{13} = 1.04 \times 10^{10} \text{ eV/\AA}, \\ \tilde{\alpha}'_{14} &= 7.15 \times 10^9 \text{ eV/\AA}, \tilde{\alpha}'_{15} = 7.07 \times 10^{10} \text{ eV/\AA}, \end{aligned}$$

for dimeric bacteriochlorophyll P^* ,

$$\tilde{\alpha}'_{21} = 3.49 \times 10^9 \text{ eV/\AA}, \tilde{\alpha}'_{22} = 6.28 \times 10^9 \text{ eV/\AA},$$

for monomeric bacteriochlorophyll B,

$$\tilde{\alpha}'_{31} = 1.49 \times 10^{11} \text{ eV/\AA}, \tilde{\alpha}'_{32} = 3.2 \times 10^8 \text{ eV/\AA}, \tilde{\alpha}'_{33} = 4.53 \times 10^9 \text{ eV/\AA},$$

for pheophytin H,

$$\tilde{\alpha}'_{41} = 1.43 \times 10^{10} \text{ eV/\AA},$$

for quinone Q_A , where

$$\tilde{\alpha}'_{ij} = \frac{\alpha'_{ij}}{\sqrt{M_{ij}/1g}}$$

and masses M_{ij} are measured in grams (g).

Though the values of masses M_{ij} are presently unknown, the parameters used in our model suffice to study the dynamics of electron transfer in a RC [17].

The newly introduced parameters α'_{32} , α'_{33} , and α'_{41} are fitting ones chosen from the condition of the best agreement between theoretical and experimental results.

5. Results of Numerical Calculations and Their Agreement with Experiment

In keeping with the method expounded in [17], we integrated numerically the system (2), (3) which determines the electron transfer dynamics in a RC (see Appendix). Figure 2 shows time dependencies of the probabilities of electron occurrences $|b_i(t)|^2$ ($i = 1$ corresponds to P^* , $i = 2$ corresponds to B, $i = 3$ corresponds to H, $i = 4$ corresponds to Q_A).

At the top of Figure 2 is shown the electron dynamics over an interval of 6 ps. It suggests that in the case of zero temperature $T = 0$ the transition of an electron to bacteriopheophytin occurs very quickly, during approximately 0.5 ps. On this time interval the monomeric bacteriochlorophyll plays the role of an intermediate: in the very first moments an electron hops to B and only after that to H. Notice that according to the results obtained, at $50 \text{ ps} \geq t \geq 0.35 \text{ ps}$, the probability of an electron occurrence at monomeric bacteriochlorophyll remains high and makes up approximately 25%.

According to Figure 2, the earliest stage of charge separation corresponding to the time interval $t \leq 1 \text{ ps}$ occurs with amplitudinous oscillations of the charge density on P^* , B and H. This leads to oscillations of the absorption bands of these active centers.

At the bottom of Figure 2 is shown the dynamics of charge transfer to quinone Q_A and its escape from bacteriopheophytin H over a time interval of 200 ps. The figure suggests that the time of the electron transition to Q_A makes up approximately 100 ps which agrees completely with experimental measurements of the electron transfer rate at helium temperatures [32]. Notice that the process of charge transfer to Q_A is also accompanied by oscillations of charge density which are clearly seen for the values of $|b_3(t)|^2$ and $|b_4(t)|^2$ at $t \approx 50 \text{ ps}$.

It is seen from Figure 2 that during rather a long time ($\approx 12 \text{ ps}$) the probability of an electron occurrence on Q_A is very small and begins growing sharply only after a lapse of this time. As the probability of an electron occurrence on H (given by $|b_3(t)|^2$) decreases, the probability of its occurrence on B (determined by $|b_2(t)|^2$) also falls down and virtually turns to zero at $t \geq 100 \text{ ps}$. The picture of electron

Figure 2. Time dependencies of electron occurrence probabilities: $|b_1(t)|^2$ – on dimeric bacteriochlorophyll (P^*); $|b_2(t)|^2$ – on monomeric bacteriochlorophyll (B); $|b_3(t)|^2$ – on bacterio-pheophytin (H); $|b_4(t)|^2$ – on quinone ($|Q_A|$) over the time intervals of 6 ps (top figure) and 200 ps (bottom figure).

transfer in the four-site model presented above somewhat differs from that in the three-site model considered in [17]. In particular, the probability of a charge occurrence on monomeric bacteriochlorophyll is greater in the four-site model than in the three-site one.

In Figure 3 we reproduce the results of [17] for the absorption curve of dimeric bacteriochlorophyll determined by the value of the electron energy modulation on

Figure 3. Time dependence of light absorption by dimeric bacteriochlorophyll P^* a) experiment [19]; b) calculated dependencies (Rhodobacter sphaeroides).

this center $\Delta E = \Delta E_1$:

$$\Delta E_1(t) = \sum_j \alpha'_{1j} q_{1j}(t) \quad (4)$$

where curve 1 in Figure 3b corresponds to the parameter values of the three-site model [17]. Curve 2 in Figure 3b corresponds to the parameter values of the four-site model (Section 4).

As is seen from Figure 3, the behavior of curves 1 and 2 matches the general behavior of the family of experimental absorption curves $\Delta A(t)$, representing oscillations of the primary processes of charge separation [19].

Figure 4. Time dependence of light absorption by bacteriopheophytin $\Delta E(t)$: Solide curve – calculations; circles – experimental values [32].

Figure 4 presents the results of numerical calculations of the time dependence of energy modulation $\Delta E(t) = \Delta E_3(t)$ determining the amount of light absorbed on bacteriopheophytin H restored as a result of primary processes of charge separation:

$$\Delta E_3(t) = \sum_j \alpha'_{3j} q_{3j}(t). \quad (5)$$

Black circles in Figure 4 show experimental values [32].

According to the results obtained, the initial fast growth of the absorption band in Figure 4 indicates formation of a reduced state of bacteriopheophytin which corresponds to arising of the absorption band of 665 nm [32]. Sharp fall of the curve beginning with $t \geq 15$ ps corresponds to commencement of the electron transition from H to Q_A , which is clearly seen in Figure 2.

Agreement between theoretical and experimental results suggests that the reaction of charge transfer from H to Q_A has adiabatic character and in the photoreaction center is determined by the dynamics of nuclear displacements (5).

6. Discussion of the Results Obtained and Possibilities for Further Development of the Theory

One of the most important results of the work is development of a unified dynamical theory of electron transfer in a RC consistent with the experiment and covering time scales from fractions of a ps to 200 ps. The theory takes into account detailed information on a RC. Thus, the data on the structure and dynamical characteristics of a RC are presented by matrix elements v_{ij} and oscillatory frequencies ω_{ij} . For

lack of thorough information on all the parameters involved, their choice remains ambiguous. A large number of parameters in the theory makes difficult its parametric investigation. It is possible that some of them will subsequently be revised or new ones will be added so as to adapt the theory to new data to be found. This, however, will not affect the main scheme of the theory of dynamical processes in a RC since it is based on fundamental equations of quantum and classical mechanics.

In terms of the approach developed, the physical picture of charge separation in a RC looks as follows. The central role belongs to oscillatory modes. Noteworthy are three important points. First, the mode relaxation (possibly partial as on monomeric bacteriochlorophyll B) in the course of electron transfer over a chain of sites P^* , B, H, Q_A in a RC leads to a decrease in the total energy of the electron + oscillatory subsystem. Effective transition of an electron from a site to a neighboring one occurs by way of tunneling only in the case when the electron energies on these sites are levelled up. So, electron transitions in the course of transfer occur adiabatically following the changes in the positions of site displacements described by quantities q_{ij} . This is the second important role of the oscillatory subsystem. Thus, for example, if we put in Equations (2), (3) the constant for an electron coupling with oscillations α'_{ij} equal to zero, the probability of an electron transition to Q_A will turn to zero. And finally, the third important role of the electron interaction with the oscillatory subsystem is in the fact that this interaction makes irreversible the electron transition to Q_A . In particular, if we put friction coefficients γ_{ij} equal to zero, Equations (2), (3) will describe a reversible oscillatory process in which an electron will periodically turn back to dimer P^* .

As we have just noted, one condition of the electron transfer requires that a portion of the electron energy should be lost in the course of tunneling. It is lost due to the electrons interaction with high-frequency oscillations of the protein light atomic groups containing hydrogen. The duration of these oscillations is some fractions of a picosecond. According to our results, it is precisely these oscillations which determine the time of transfer at the stage of transition from P^* to H. Detailed information on the nature of these oscillations is presently lacking. Thus, according to [33], oscillations at the frequency of 15 cm^{-1} include motions of the RC protein which modulate positions and orientations of P and B relative to each other. Oscillatory frequencies of a water molecule localized near the dimeric bacteriochlorophyll fall in the same frequency range [27, 28]. The origin of other dominating frequencies has not been revealed unambiguously. For the dominating frequencies of 12 cm^{-1} and 30 cm^{-1} associated with the electron transfer, which were determined in [19] from oscillations of the absorption band only for low frequency mode can be ascribed the same nature as for 15 cm^{-1} frequency [33]. Molecular dynamics simulations of the RC, on the other hand, revealed several classical vibrational modes with frequencies of $20\text{--}100\text{ cm}^{-1}$ altering the electrostatic energy gap of the $P^*B \rightarrow P^+B_A^-$ which lies in the range of our frequency parameters [33]. Displacements of oscillating nuclei from equilibrium positions in this case are insignificant: $\sim 10^{-2}\text{ \AA}$.

On the contrary, electron transfer from H to Q_A is mainly determined by the slowest oscillations – in our case ω_{32} – which may include structural changes in the protein as well. Displacements of nuclei in a protein molecule which accompany its structure reconstructions are larger than 10^{-2} Å and approach 1–2 Å. The gain in energy caused by electron interaction with slow oscillations appears larger than in the case of high-frequency oscillations and for the transition $H^- Q_A \rightarrow H Q_A^-$ can be as large as 0.3–0.4 eV.

Comparison of Figures 2 and 3 suggests that the time of electron transfer per se is shorter than that obtained from measurements of the absorption spectra. The reason is that atomic nuclei deviate from their equilibrium positions with some delay since their motion is determined by classical motion Equations (3). This effect is especially pronounced in the transitions of $P^* B \rightarrow P^* B^-$ and $B^- H \rightarrow B H^-$. It follows from Figure 2 that these transitions are very fast: ~ 0.5 ps. On the other hand, the time of transition $B^- H \rightarrow B H^-$ determined from the initial region of the absorption curve for pheophytin H in Figure 4 yields the transition time (i.e. arising of the absorption band of 665 nm) of 1.5–2 ps which agrees completely with experimental data [34].

The phenomenon of delayed arising of absorption bands accompanying electron transfer makes the elucidation of the details of the very first stages of charge separation when the time of an electron occurrence on an intermediate is very short very difficult. In particular, it makes difficult the solution of the problem of whether “at the initial stage” an electron passes on from P^* to B or a more complicated process takes place where a water molecule acts as an intermediate [27, 28].

In conclusion, it may be said that the processes of electron transport as part of photosynthetic primary processes present a unified multilevel system characterized by a hierarchy of times, frequencies, interaction constants and peculiarities of the structure organization of its constituents in the photosynthetic membranes. All this makes the photosynthetic electron transport system one of few biological systems for which optimum mathematical models can be built with modification of parameters and experimental testing of their adequacy to a real modeled object.

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Appendix

The transfer to dimensionless variables used for integration of system (2), (3) is made by relations [17]

$$\begin{aligned} \eta_i &= \eta_{ii} = \tau \alpha_i / \hbar; & \eta_{i,i'} &= \tau v_{i,i'} / \hbar; \\ \tilde{\omega}_{ij}^2 &= \tau^2 K_{ij} / M_{ij}; & \kappa_{ij} \tilde{\omega}_{ij}^2 &= \tau^3 (\alpha'_{ij})^2 / M_{ij} \hbar; \\ \beta_{ij} &= \tau^2 \alpha'_{ij} / M_{ij}; & t &= \tau \tilde{t}; & q_{ij} &= \beta_{ij} u_{ij}. \end{aligned}$$

In dimensionless variables Equations (2) and (3) take the form:

$$i \frac{db_n}{d\tilde{t}} = \eta_n b_n + \eta_{n,n+1} b_{n+1} + \eta_{n,n-1} b_{n-1} + \sum_j \kappa_{nj} \tilde{\omega}_{nj}^2 u_{nj}$$

$$\frac{d^2 u_{nj}}{d\tilde{t}^2} = -\tilde{\omega}'_{nj} \frac{du_{nj}}{d\tilde{t}} - \tilde{\omega}_{nj}^2 u_{nj} - |b_n|^2.$$

For $\tau = 10^{-14}$ s, and parameters introduced in Section 4, the dimensionless values are:

matrix elements: $\eta_{11} = 0$; $\eta_{12} = 0.15$; $\eta_{21} = 0.15$; $\eta_{22} = -0.2$; $\eta_{23} = 0.15$;
 $\eta_{32} = 0.15$; $\eta_{33} = -0.32$; $\eta_{34} = 0.65$; $\eta_{43} = 0.65$; $\eta_{44} = -5.9$;
 coupling constants: $\kappa_{11} = 0.25$; $\kappa_{12} = 0.05$; $\kappa_{13} = 0.05$; $\kappa_{14} = 0.015$; $\kappa_{15} = 0.32$;
 $\kappa_{21} = 0.58$; $\kappa_{22} = 0.3$; $\kappa_{31} = 0.48$; $\kappa_{32} = 5$; $\kappa_{33} = 4$; $\kappa_{41} = 0.5$;
 frequencies: $\tilde{\omega}_{11} = 0.0283$; $\tilde{\omega}_{12} = 0.173$; $\tilde{\omega}_{13} = 0.23$; $\tilde{\omega}_{14} = 0.288$; $\tilde{\omega}_{15} = 0.616$;
 $\tilde{\omega}_{21} = 0.0226$; $\tilde{\omega}_{22} = 0.0566$; $\tilde{\omega}_{31} = 1.063$; $\tilde{\omega}_{32} = 0.0007$; $\tilde{\omega}_{33} = 0.1$; $\tilde{\omega}_{41} = 0.1$;
 damping frequencies: $\tilde{\omega}'_{11} = 0.04$; $\tilde{\omega}'_{12} = 0.02$; $\tilde{\omega}'_{13} = 0.025$; $\tilde{\omega}'_{14} = 0.027$;
 $\tilde{\omega}'_{15} = 0.5$; $\tilde{\omega}'_{21} = 0.1$; $\tilde{\omega}'_{22} = 0.1$; $\tilde{\omega}'_{31} = 1.12$; $\tilde{\omega}'_{32} = 0.01$; $\tilde{\omega}'_{33} = 1$; $\tilde{\omega}'_{41} = 0.1$.

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