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A theoretical model for electron and proton coupling at quinone-binding site of photosystem II of higher plants

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Abstract

In this work we consider the coupling of electron and proton transfer near Q_B in the reaction center (RC) of photosystem II (PS2). We have carried out the calculations of the energy levels and proton density in the system Q_B^- Histidine L190. It is shown that the proton of the histidine forms the H-bond with twice-reduced Q_B^{2-}. Based on these calculations, we propose a new explanation of the coupling between the electron and proton transfer.

Keywords: Plastoquinone; Electron and proton transport; Photosystem II

1. Introduction

The membrane protein-pigment complexes called the RC play a major role in the energy transduction in photosynthesis. In the RC of purple bacteria and in the RC of photosystem II of higher plants after the transition of the chlorophyll special pair to the excited state the electron of the special pair is transferred to the primary quinone Q_A via bacteriochlorophyll (or chlorophyll in plants) and bacteriopheophytin (or pheophytin in plants) and then the electrons go to the secondary quinone, Q_B. During the electron transport in these reaction centers, Q_A acts as a single electron carrier while Q_B can accept two electrons. After the reduction by two electrons, Q_B is transformed to Q_BH_2, detaches from its binding site (the so-called Q_B-pocket) and diffuses to the cytochrome b_6f-complex. The empty Q_B pocket is reoccupied by oxidised Q_B from the intra-membrane space.

The discovery of the X-ray structure of the reaction center (RC) of the purple photosynthetic bacteria made possible to consider the molecular mechanism of the coupling between the electron and the proton transport near Q_B, the secondary quinone in these RC. Numerous studies of this reaction permit to suppose that in this process an important role is played by the quantum properties of Q_B and the surrounding molecules. Now, in literature, two problems concerning the electron and proton transfer and the function of Q_B are generally discussed. The first problem is which electron characteristics of Q_B in different redox-states are essential for its docking to and detachment from its binding site and also for proton transport across the membrane? The second problem concerns the mechanism of synchronization between the Q_B reduction and the proton transfer from the outer membrane space. The last question is what role do the movements of Q_B in its binding site, discovered in Ref. [1], have in the coupling between the electron and proton transfer?

Let us formulate the problems concerning the Q_B function in the reaction center that remain unsolved up to now. It is necessary to note that the nature of the spontaneous conformational changes in the RC facilitating the electron transfer to Q_B remains unclear. Thus, it is unknown which "energy supply" is used for the movement of such relatively large molecules as the quinones or their fragments. Also, it remains unknown why these conformational changes could not be revealed from the spectral properties of RC, investigated in detail in wide temporal interval from 100 femtoseconds to several seconds. And, finally, what is the physicochemical mechanism of synchronization between the electron transfer for the Q_B reduction and the proton absorption from the outer membrane space of the chloroplasts?

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Earlier we have supposed that the proton transfer occurs by the proton movement from His L190 to oxygen of Q_B [2]. In order to verify this assumption, we have calculated the energy of the Q_B–His system for different proton positions between them for different states of Q_B (neutral, singly reduced and twice reduced). Basing on the analysis of the obtained energetic curves, we have made an assumption about the formation of H-bond in case of singly reduced quinone and the formation of covalent bond between the proton and the twice-reduced quinone. The formation of these bonds gives rise to the changes in the distance between His L190 and Q_B [2,3].

In the present work, we have determined the probability density for proton positions between His and Q_B, numerically solving the Schrödinger equations for proton in His–Q_B system. We believe that the transfer of first the two electrons and then the proton from the His L190 to the quinone Q_B may be considered as a model of the primary stage in the coupled electron and proton transfer in the RC of purple bacteria and possibly the RC of PS II of higher plants.

2. Experimental

The calculations of the probability density for the proton position and corresponding energy levels have been performed using the system MATLAB. The special program for numerical calculations of Schrödinger equation was developed.

Mathematically considered, the solution of the Schrödinger equation is an eigenvalues and eigenfunctions problem—the Sturm–Liouville problem. The usual difference methods of numerical analysis can thus be applied to the Schrödinger equation. The details of calculations and the corresponding references are described in Ref. [3].

3. Results and discussion

Supposing that the His proton can move along the direct line connecting the nitrogen atom (to which it is initially covalently bonded) and the nearest oxygen of the quinone, we have calculated the probability density of its position as a function of its distance to the His nitrogen for different states of PQ (oxidized, singly reduced, and twice reduced) and for different distances between the His and the quinone (from the His nitrogen to the quinone oxygen). The obtained squares of the wave function (the probability densities for the proton positions along the direct line N–O) and the corresponding energy levels are presented in Figs. 1 and 2. In Ref. [2], the total energy of system PQ–His was calculated for different N–H...–O for range from 0.2 to 0.5 nm. In this work, we have chosen the two specific distances between the His and the quinone which is equal to 0.25 (Fig. 1) and 0.5 nm (Fig. 2). In the first case (0.25 nm), we have the wide potential wells. In the second one (0.5 nm) the narrow potential wells are separated form each other by great potential barriers.

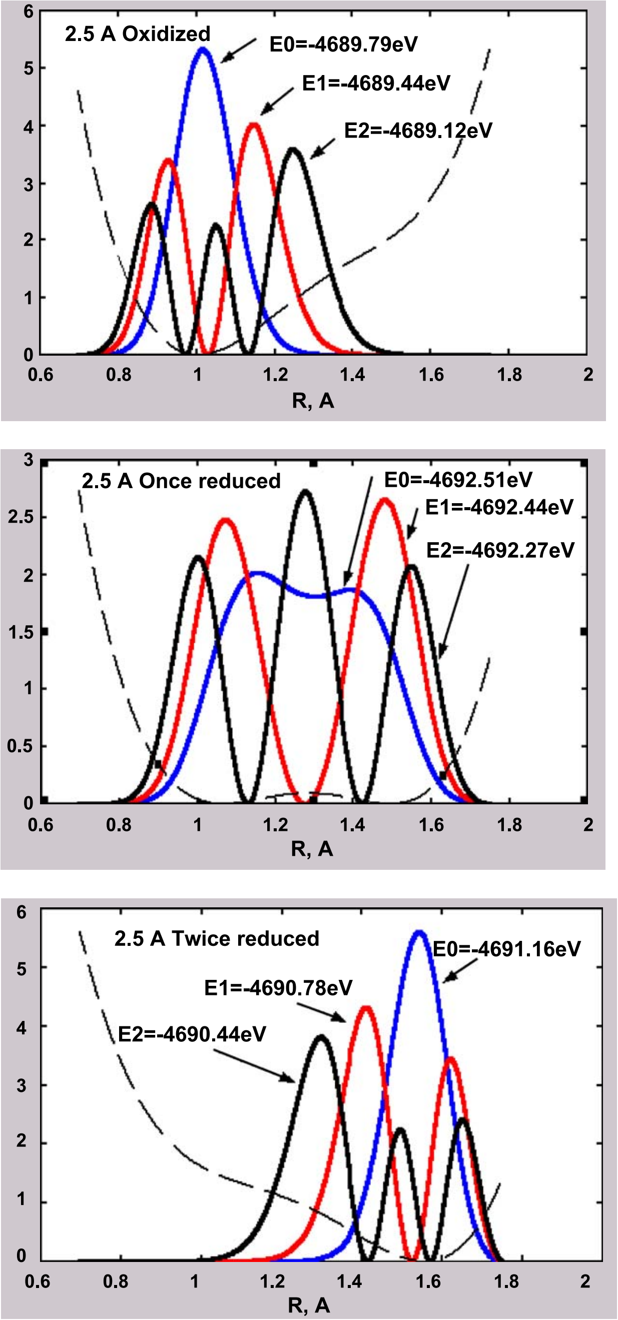

Fig. 1. Dotted line—The total electronic energy of His and PQ in different redox states for the different distance R between proton and nitrogen atom; solid lines—the squares of wave functions of proton; the corresponding energy levels for proton movement are indicated by arrows. N–H–O distance is equal to 2.5 Å.

It should be noted that the dependences of the total energy system on the proton position can show either one or two deep potential wells. The results of the calculations for the first type of curves (the distance R(O–H...N) equals 2.5 Å) are presented in (Figs. 1 and 2).

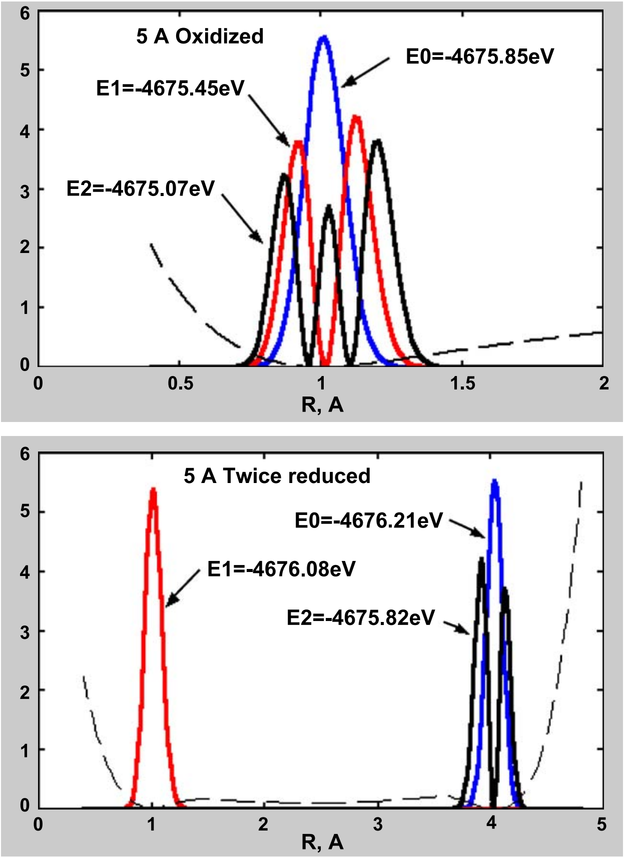

Fig. 2. Dotted line—The total electronic energy of His and PQ in different redox states for the different distance R between proton and nitrogen atom; solid lines—the squares of wave functions of proton; the corresponding energy levels for proton movement are indicated by arrows. N–H–O distance is equal to 5 Å.

For the oxidized PQ (Fig. 1) the only maximum of the probability density is localized near the nitrogen atom of His. The maxima of the excited functions are in no more than 0.5 Å from this position. The probability density of the ground state for singly reduced quinone, PQ^{-} (Fig. 1), is localized in the middle between the nitrogen of His and the oxygen of PQ. The maxima of the probability density for the excited states are apart from each other. Such localization of proton indicates that the H-bond forms. For twice-reduced quinone, PQ^{2-} (Fig. 1) the maximum of the probability density for the ground state lies in the range 0.9 Å from the oxygen atom of PQ, indicating the formation of a covalent bond.

In Figs. 1 and 2, it can be seen that the shift of the proton probability density from the nitrogen of His to oxygen atom of PQ takes place upon the reduction of PQ. It should be noted that the energy difference between the ground and the first excited levels is larger than the energy of the translational movement of the molecules at the room temperature (0.025 eV). It means that it is impossible to excite our system to the first excited level.

The details of the calculations for the energetic curves with two deep maxima are presented in Fig. 2 for the distance R(N–H...O) equal to 5 Å. The probability distribution of the proton coordinate is practically the same as in previous case, that is for the energetic curve with the one well. The probability density for the first excited level of twice-reduced PQ_B has a maximum that is localized near His. The probability density for the second excited level is again located near the oxygen of Q_B. So it alternates while the number of the level increases. The probability density of the ground level has the maximum located in 1 Å from the oxygen of Q_B. On the basis of the energetic difference between two levels, it is possible to estimate the vibrational frequency of proton movement in the system under consideration. This value is about 3000 cm^{-1}, which corresponds to the experimental data by an order of magnitude [3].

Although in Ref. [4] the authors have studied the capacity of aminoacids surrounded of PQ to give the proton using the estimation of pK, these values were obtained using thermodynamic approaches. In the present work, we have investigated the capacity of His to give the proton to plastoquinone by quantum-chemical method using the data on the molecular structure of PQ–His complex. Thus, we have shown that in the quinone–Histidine system, the redox state of the quinone determines the proton position between the His nitrogen atom and the oxygen atom of the quinone. We think that this circumstance is of importance for understanding the synchronization of Q_B reduction and proton absorption from the outer membrane space of higher plants thylakoids. It should be noted that the approach to the calculation of energy for different proton positions we have used in Ref. [5] and in this article was first proposed by Salem in Ref. [6]. Using the virtual charge method the author has calculated the energy of two water molecules and obtained an energetic curve with two potential wells. In our work we have applied the similar approach to clarify the formation of H-bond, and the covalent bond between the molecules of PQ_B and His L190 in bacterial RC and possibly in the RC of higher plant PS II. Similar curves were postulated in Ref. [7] without the energy calculation as a quantitative illustration of pK_a proton donor group effect on the characteristic of H-bonds in oxygen evolving system of the higher plants. As a result of analysis carried out in our work it can be proposed that one of the protons of the hydroquinone PQ_BH_2 was detached from His L190. It occurs because the proton donor group of His L190 is located considerably nearer to Q_B oxygen than the proton donor groups of other aminoacids that could donate the protons to the twice-reduced Q_B (Ser L223, Asp L213 or Glu L212).

Such assumption about the way of proton transfer permits us to propose the following new scenario of coupling of electron and proton transfer near Q_B:

1. The cycle begins with the electron tunneling from Q_A^- to Q_B via the nonheme Fe and His L190. Q_B is reduced to a semiquinone Q_B^-. Q_B^- attracts the proton from His L190

so that it is now positioned in the middle between the nitrogen of the His L190 and Q_B oxygen, forming a H-bond.

2. A second electron passes from Q_A to Q_B. The proton forming the H-bond shifts to the PQ oxygen and forms a covalent bond with it.
3. A proton from the nearest aminoacid (perhaps Ser L223) shifts to the opposite oxygen of PQ_B, forming a covalent bond. During this process the electron density shifts to this oxygen and the proton bound with the opposite oxygen passes to His, forming covalent bond. In doing so, His L190 restores the initial neutral state.
4. The twice-reduced quinone Q_B with one proton attached rotates by 180° around its isoprene tail. The unprotonated oxygen of Q_B moves to another proton donor aminoacid (Asp L 213 or Glu L 212), "tears" the proton off from the proton donor group and forms a covalent bond with it. It is important to note that the proton channels from outer membrane space lead to Asp L 213, Glu L 212, Ser L223 aminoacids, whereas His L190 is not linked by the proton channels with outermembrane space.
5. The lacking protons of the proton donor groups of the aminoacids are replaced by external protons from the outer membrane space through the proton channels. After that, the affinity of Q_BH_2 to the binding site decreases, and Q_BH_2 leaves this site and is replaced by neutral Q_B. The cycle of Q_B is over.

4. Conclusions

Let us remind the new moments in this work comparing to the previous studies. First, we suppose that His L190 plays an essential role in the electron–proton coupling. Second, we explain the necessity of PQ_B rotation by 180° around its tail for the shift of unprotoned Q_B oxygen to the aminoacids (Asp L 213 or Glu L 212) linked with outer membrane space by the proton channels. In conclusion, it should be noted that on the basis of results obtained it is possible to calculate the proton transfer rate from outer membrane space to PQ_B and compare it to the experimental data. We hope to make it in the future.

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