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Geometric phase and quantum interference in photosynthetic reaction center: Regulation of electron transfer

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ABSTRACT

Photosynthesis is driven by electron transfer in reaction centers in which the functional unit is composed of several simple molecules C_2-symmetrically arranged into two branches. In view of quantum mechanism, both branches are possible pathways traversed by the transferred electron. Due to different evolution of spin state along two pathways in transmembrane electric potential (TEP), quantum state of the transferred electron at the bridged site acquires a geometric phase difference dependent on TEP, the most efficient electron transport takes place in a specific range of TEP beyond which electron transfer is dramatically suppressed. What's more, reaction center acts like elaborately designed quantum device preparing polarized spin dependent on TEP for the transferred electron to regulate the reduction potential at bridged site. In brief, electron transfer generates the TEP, reversely, TEP modulates the efficiency of electron transfer. This may be an important approach to maintaining an appreciable pH environment in photosynthesis.

1. Introduction

Virtually living things on planet are directly or indirectly dependent on photosynthesis that produces atmospheric oxygen and food utilizing light. This energy conversion from light to stable chemical form is conducted by some integral protein-pigment complexes embedded in membrane where photons are captured by light-harvesting systems and then are transferred in form of excitation energy to reaction centers (RC) to drive transmembrane charge transfer. Accompanying charge transfer, a proton-motive force is established across membrane for synthesis of ATP. To adapt to living environment, distinctive composition and architectures have been developed for light-harvesting systems of different photosynthetic species [1–4]. But it is particularly interesting that RCs including photosystems I and II of cyanobacteria, green algae and plants, as well as purple bacteria, are all characteristic of two symmetric branches of electron transfer co-factors. As shown in Fig. 1, a special pair of chlorophyll (bacteriochlorophyll) (SP) denoted as P_A and P_B locates at lumenal side of membrane, from which two branches of molecular co-factors spreads towards stromal side. Each branch comprises of two chlorophyll(bacteriochlorophyll) (A_1 and A_2 for A branch and B_1 and B_2 for B branch) and one quinone (A_3, B_3). Finally they meet at a bridged site F which is a Fe_4S_4 cluster (type I) or a Fe ion (type II).

In the last decades, RCs have been extensively studied using various techniques concerning on kinetics and mechanisms of electron transfer, and a huge body of literature has been published [5–12]. However, little attention was payed to the special structure preserved by all photosynthetic species after billions of years of evolution, particularly, the relationship between such structure and electron transfer. This issue is of fundamental importance to understand photosynthesis, but also important to improve both natural and artificial photosynthetic systems for benefit of the human race. This work will focus on the potential significance of that special structure of RCs in view of quantum mechanism.

It sounds somewhat weird that quantum mechanism plays roles in photosynthesis conducted by complicated pigment-protein complex in wet and ambient environment, but studies in recent years provide convincing proofs that nature in fact develops tricks using principles of quantum realm. In 2007, quantum coherence over appreciable length scales and time scales in the Fenna–Matthews–Olson [13] was first observed by a group under Graham Fleming at low temperature (77 K). Since then a large number of researches were published [14–17] suggesting that the coherence is non-negligible even at room temperature for up to 300 fs. Such quantum coherence is supported by the strong electronic coupling among pigments and their tight binding to intrinsic protein environment that protects involved pigments from solvent

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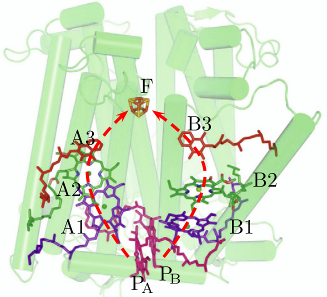

Fig. 1. Geometric arrangement of electron-transfer co-factors in the photosynthetic reaction center. The chlorophyll P_A and P_B forms the special chlorophyll pair, P700. Co-factors denoted by A_1, A_2, B_1 and B_2 are all chlorophylls, while A_3 and B_3 are phylloquinones. These six molecules are arranged into two electron transfer branches, A and B, which are bridged at magnetic cofactor, F.

molecules. In the case of RC, the functional components are embedded in a protein cavity of nanometer scale in which only several water molecules are found in form of hydrogen-bond according to X-ray crystal structure. The coupling between chlorophyll constituting SP seems to be the strongest, and long-lived quantum coherence has been observed among electron transfer co-factors [17,18].

The symmetric geometry of RC is helpful to reduce influence of environment. Structurally, the C_2-symmetric electron transfer chain is analogous to a Mach–Zehnder interferometer in quantum optics [19]. Two branches are both possible pathways for the transferred electron. Assume that $|\Psi_A\rangle = |\psi_A(\mathbf{r})\rangle \otimes |\chi_A\rangle$ and $|\Psi_B\rangle = |\psi_B(\mathbf{r})\rangle \otimes |\chi_B\rangle$ are quantum states of an electron traveling along those two pathways, respectively, in form of product state of the spatial state $|\psi(\mathbf{r})\rangle$ and internal spin state $|\chi\rangle$. By including the environmental states of two branches, $|e_A\rangle$ and $|e_B\rangle$, the interference at bridged site is written as

$$\langle\Psi|\Psi\rangle = |a|^2 + |b|^2 + 2Re[a\,b\langle\Psi_A|\Psi_B\rangle\langle e_A|e_B\rangle]\cos\Theta \tag{1}$$

here a and b are superposition factors, and Θ is phase difference due to different evolution along two branches. If the difference between the effects of taking branches A and B on the environment is small, the interference is conserved, otherwise, $|e_A\rangle$ and $|e_B\rangle$ are orthogonal and the state reduces to the incoherent mixture. Allowing for the identical component and similar protein environment, $|e_A\rangle$ differs from $|e_B\rangle$ slightly, and the quantum interference may take place with big possibility.

The interference described by Eq. (1) is in fact sensitive to physiological situation. The proton-motive force generated by transmembrane charge transfer is partially stored in form of transmembrane electric potential (TEP). Moving in TEP, spin of the transferred electron couples with electric field corresponding to TEP, and its state evolves differently along two branches of electron transfer chain contributing a geometric phase [20,21] difference in Θ of Eq. (1). It is shown in this work that the strongest interference occurs in a specific range of TEP beyond which it dramatically decreases. Spin state of the transferred electron is also affected by the electrostatic field produced by environmental molecules, but the contribution to Θ is static and independent of TEP due to stable geometric structure of RCs. Recently, Naaman's group observed spin polarization in monolayers of a photosystem I, and spin of radical SP^+ is well correlated with that of the separated electron [22]. What's more, long-lasting coherence has been observed in reaction center [18,17], the charge-separated radical pair of the primary electron donor and acceptor appears in the spin-correlated state which response of electron-paramagnetic-resonance displays features of spin-polarization and quantum beats [10–12]. These results apparently indicate that quantum mechanism plays an important role in electron transfer in RCs.

Dependence of electron transfer on TEP not only makes the special structure of RCs meaningful, but also introduces important roles in photo-protection and maintaining appreciable pH for enzymes. Accompanying electron transfer, reactive oxygen species such as hydrogen peroxide (H_2O_2) and oxygen in singlet state ($^1O_2$) are produced causing damage to photosynthetic organisms [23]. Though different mechanisms have been suggested to avoid oxidative stress, none of them is related to the source, electron transfer in RCs. Now that electron transfer is sensitive to physiological situation, TEP, photo-protection will be more efficient with faster response to excess light. In photosynthesis, synthesis of ATP is driven by H^+ arising from electron transfer, but this does not mean the higher concentration of H^+, the more ATP produced, because enzymes involved in photosynthesis act most actively under specific pH [24–26]. Physiologically, the light-induced acidification of the thylakoid lumen causes a slowing down of electron transfer in the cytochrome b_6f segment of photosynthetic electron transfer chain [27] possibly due to back "pressure" of protons accumulated inside thylakoid. This process takes place in time of *ms* scale while the electron transfer occurs in time of *ns* scale. Obviously, regulation of electron transfer between PSI and PSII is not the most efficient mechanism. The dependence of electron transfer in RCs on TEP proposed in this work makes performance of RCs be naturally modulated as an engine of photosynthesis by means of state evolution of the transferred electron in TEP, the rate of electron transfer is regulated by TEP and a suitable concentration of H^+ is maintained.

It should be pointed out that though only one branch is observed active in RCs of purple bacteria and photosystem II, modulation through TEP is still valid. Firstly, electron transfer of photosystems I and II are connected in the so-called Z scheme [28] in which electrons from RC of photosystem II flow through a series of intermediates to the RC of photosystem I. Therefore, electron transfer in photosystem II will be blocked if that in photosystem I is suppressed. Secondly, spin is polarized when an electron moves in TEP, its interaction with the bridged co-factor then becomes related to TEP. This means that reduction potential at bridged co-factor is regulated according to physiological situation too.

In this article, the state evolution in TEP and the acquired geometric phase are first described, then numerical results about spin polarization and dependence of electron transfer on TEP are given.

2. Theory and methods

The Hamiltonian of an electron moving in TEP [20] is

$$\hat{H} = \frac{1}{2m}\left(\mathbf{p} - \frac{\mu}{2c}\boldsymbol{\sigma}\times\mathbf{E}\right)^2 + V(\mathbf{r}) \tag{2}$$

with Pauli vector operator $\boldsymbol{\sigma}$, Bohr magneton μ, and the spin independent local potential $V(\mathbf{r})$ at position $\mathbf{r}$. Following Zhu and Wang [29], its quantum state can be constructed using ψ_0 of Hamiltonian

$$\hat{H}_0 = \frac{(-i\hbar\nabla)^2}{2m} + V(\mathbf{r}) \tag{3}$$

as $\psi = \hat{U}^{-1}\psi_0$. The TEP contributes a phase factor defined by

$$\hat{U} = \hat{P}\exp\left(\frac{i\mu}{2\hbar c}\int(\sigma\times\mathbf{E})\,d|\chi\rangle\right) \tag{4}$$

with $\mathbf{E}$ the transmembrane electric field, c the light speed, and $\hat{P}$ the path ordering operator. This phase factor is determined by a Schrödinger-type equation

$$i\hbar\frac{\partial}{\partial l}|\chi(l)\rangle = \frac{\mu}{2c}\boldsymbol{\sigma}\cdot(\mathbf{e}_v\times\mathbf{E})|\chi(l)\rangle \tag{5}$$

with variable l the relative distance, $\mathbf{e}_v$ the unit vector of the speed of the transferred electron.