Quantum Mechanics in Photosynthesis

Frank Jones

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Photosynthesis is the process that plants use to convert water and carbon dioxide into energy. The sequence of events that produce glucose and oxygen can be broken up into two stages, the light reaction, and the dark reaction. During the light reaction, sunlight excites electrons in chlorophyll. These excited electrons are transported to the reaction center to begin chemical reactions that will produce ATP. In the dark reaction, ATP is used to create carbohydrates which provide food for the plant. This paper will discuss the quantum properties involved in the light reaction. These properties involve quantum tunneling and quantum coherence.

1 Quantum Coherence in Exciton Energy Transfer

When a photon strikes a chlorophyll in a plant, an electron is excited to a higher energy level, known as an exciton. The incoming photon is captured by the light harvesting antennae and the excited energy is transferred to the reaction center through an exciton transport chain. Over the course of several billion years, nature has managed to make this energy transfer process known as Exciton Energy Transfer, extremely efficient. The efficiency of transmitting this energy through the cell can reach near 100 percent. For comparison, modern solar cells reach an efficiency of around 15 percent[10].
According to the Forster model, the excitation energy can be transfered from site to site through a series of incoherent jumps. The jumps take place from states of higher energy to lower energy, following a potential funnel similar to that which is believed to aide protein folding. In this manner, the exciton energy can be transmitted through the membrane.

New research addressing the efficiency of this process, however, suggests quantum coherence may play a large role in the energy transfer.
In green sulfur bacteria the antennae and the reaction center are connected by the Fenna Matthews Olson(FMO) Complex. The FMO trimer consists of 3 monomers which contain 7 densely packed chlorophylls(pigments/chromophores). This complex transmits the excitation efficiently to the reaction center. The exciton enters the monomer(depicted in Figure 2) through pigments 1 or 6, which are positioned closest to the antenna and exits through pigments 3 or 4 which are

located near the reaction center. The exciton enters the complex and samples multiple pigment paths moving like a quantum walker. The quantum walker, unlike the random walker, diffuses through the system in a super position of left and right directions resulting in a higher probability of being found at the edges of the system. This is in contrast to the random walker which moves left or right and produces a Gaussian curve centered at the origin. The exciton is guided by an energy landscape that funnels to the reaction center.

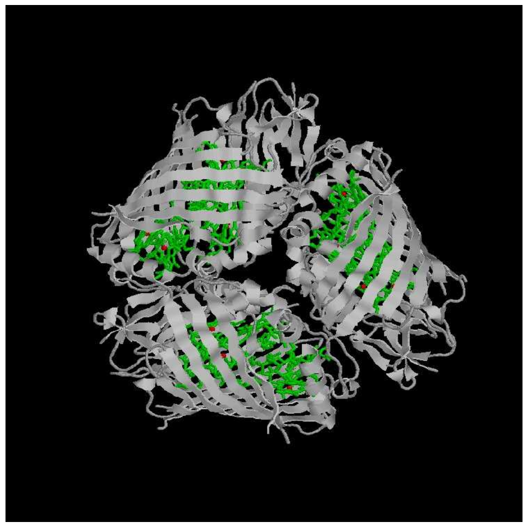

Figure 1. FMO Complex.

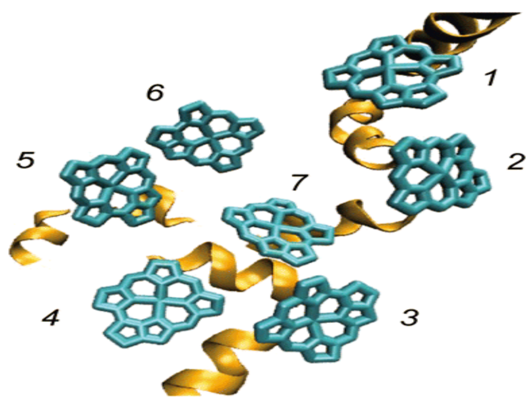

Figure 2. Seven densely packed pigments in FMO monomer.

To look for coherence in the EET process, a two-color electron coherence photon echo technique was developed which would allow the visualization of the dephasing of coherent states in the photosystem. Two initial laser pulses create an optical coherence in the first and second excited states. If these two states are mixed when a third laser pulse is applied, a photon echo signal is

recorded which is related to the dephasing of the coherent states.
What does coherence mean for efficiency? The coherence of the exciton state means that the exciton can sample multiple pathways of the energy landscape simultaneously and determine the most efficient route. This results in an efficient energy transfer process. The coherence time for this process was measured to be longer than 660fs at room temperature.

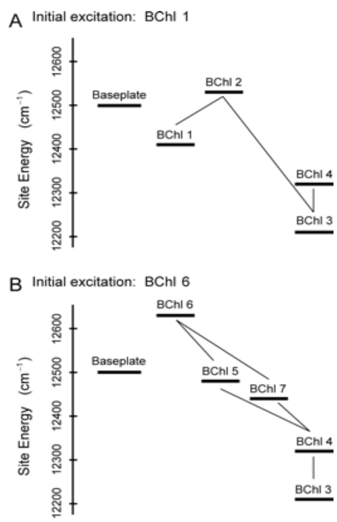

Figure 2. Pigment Energy landscape.

The amount of quantum effects observed in a system can be characterized by two values. The rate of interaction with the system, J, describes the amount of superposition between states, the formation of a quantum state. The rate of interaction with the environment, λ, determines the decoherence of these superpositions to classical values. The ratio $\frac{J}{\lambda}$ determines the amount of quantum mechanical effects occurring in a system. The FMO complex maximizes quantum coherence in several methods. Firstly, since the complex is embedded within a membrane, it exists in a controlled environment, limiting its interactions with the outside environment. Secondly, the protein cage surrounding the pigments helps to shield the system from the environment further. Both of these factors help to minimize λ. In addition, the density of the chlorophyll inside the pigment increases interactions within the system which increases J. These three factors together increase the quantum effects of the system creating long coherence times.
Coherence does not directly effect the efficiency of the energy transfer process, however. The exciton transfer process only takes a few picoseconds to complete but the coherence allows for an efficient pathway to be found. Liang additionally concludes that the environment also restricts the transfer of energy backwards up the chain, which directly effects EET efficiency by forcing the energy to reach the reaction chamber.[2]

2 Electron Transport

The electrons, excited in chlorophyll by the captured photons, must be transported from outside the mitocondria, the periplast, to the interior, the cytoplasm. To do this, they must pass through a membrane on the order of 40 angstroms wide. This sequence of events, known as the photosynthetic reaction center, is greatly facilitated by membrane proteins that penetrate the membrane and help move the electron through the cell.
Piercing the membrane are three proteins which form a hole that insulates the pigments that carry the electron. The L, M, and H membrane proteins all take the shape of α-helices and span the width of the membrane. Inside the membrane channel there are four pigments which transport the electron through to the interior of the cell. These first of these chlorophylls produces the electron when excited by photons. The electron is then transported to the accessory chlorophylls(B_A), followed by the pheophytins(P_A), and then the quinones, Q_A and Q_B, before being brought into the cell.

This process, which would be impossible without the effects of quantum tunneling, takes only a fraction of a second to complete.

3 Quantum Tunneling in Photosynthesis

The pigments which carry the electron through the membrane never actually touch eachother. Instead, electron transport is accomplished through tunneling, where the electron jumps from one pigment to another while making its way into the cell. Each pigment along the chain can be thought of as a potential well. As we know, the wave function of an electron in a finite potential well protrudes into the forbidden high potential region where it decays exponentially.

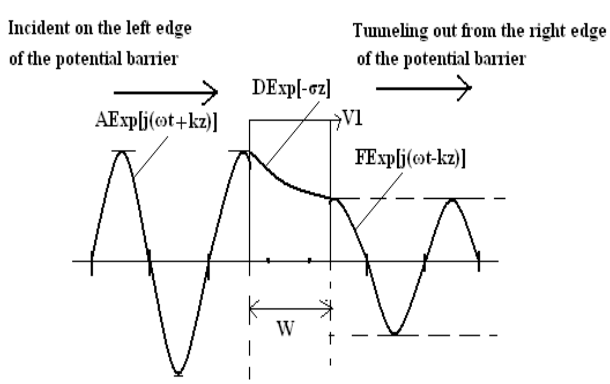

Figure 4. Electron wave function tunneling through potential barrier[6].

3.1 Transfer Matrix

The wave function of an electron in a finite potential well takes the form:

$$\Psi(x) = A\exp^{ikx} + B\exp^{-ikx} \tag{1}$$

for each section of the well. If the energy of the electron is such that the asymptotic potentials of the well are larger, the coefficients of the wave functions can be determined by

$$\begin{bmatrix} A \\ B \end{bmatrix} = E_1^{-1}K_1^{-}1K_2E_2 \begin{bmatrix} C \\ D \end{bmatrix} = T_{01} \begin{bmatrix} C \\ D \end{bmatrix} \tag{2}$$

where T_01 is the transfer matrix from the left asymptotic potential to the well. Similarly, the coefficients between the well and the right asymptotic potential are related by the T_{12} matrix. The probability of electron transmission is determined by the inverse of the (1,1) index of the transfer matrix. For this potential, where E ¡ V,

$$t_{11} = cosh\kappa\delta - \frac{i}{2}(\frac{-\kappa}{k} + \frac{k}{\kappa})sinh\kappa\delta \tag{3}$$

$$T(E) = \frac{1}{t_{11}} = \frac{1}{1 + \frac{1}{4}(\frac{\kappa}{k} + \frac{k}{\kappa})^2 sinh^2\kappa\delta} \tag{4}$$

For an electron in a potential well such as our pigment, a distance of 1 angstrom outside of the well corresponds to a 10 fold decrease in the electron's probability[4]. The electron vibrates at visible light frequencies, which for blue(which the chlorophyll absorbs most readily) is about $6x10^{14}$ Hz. To tunnel a distance of 1 angstrom would take $6x10^{-14}/10^{-1} = 6x10^{-13}$ seconds. The thickness of the membrane is about 40 angstroms. The probability of an electron tunneling this distance is then 10^{-40}.[4] In other words, it would take about 10^{16} years for the electron to make this jump, not the fraction of a second observed. Luckily, the four intermediate pigments allow the electron to make a series of shorter jumps, which decreases transmission time exponentially. If the pigments are equally spaced throughout the membrane, then the electron only has to make a series of 4, 10 angstrom jumps. This process will take around $4x10^{-5}$ seconds, which is much closer to the observed time.

4 Preventing the Back Flow of Electrons

Once the electron has made a jump from one pigment to another, what is stopping it from jumping back up the pathway? The protein structure can make conformational changes to reach its lowest energy state. When an electron enters a pigment, the conformation of the protein changes. Furthermore, each successive jump corresponds to a lower energy well. Because of this, the transition backwards has a much less probability, and the chain will continue forwards.

5 Conclusion

As we have seen, quantum mechanics being found to play an increasingly important role in the photosynthetic process. It allows energy transfer processes to reach incredibly high efficiencies that modern technology has yet to reach. This efficient process is possible through quantum coherence which allows excitation energy to sample multiple pathways simultaneously to determine the most efficient path. Furthermore, quantum tunneling effects allows excited electrons to penetrate a membrane in a biological time frame (a fraction of a second instead of years). This process allows plants to convert light energy into carbohydrates, fueling plant life. Research in this area has opened many possibilities in the field of quantum biology, and may shed light on a method of producing efficient solar cells to power the future.

6 References

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