Photoinduced Quantum Tunneling Through a Model of Square Wells Potential

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Abstract. The paper proposes a photoinduced quantum tunneling model of electron transfer through four quantum square wells potential to simulate the biological process of photosynthesis in bacteria. The problem is mathematically exact, given the cyclic process, with mathematical transcendental equations solved graphically. This simplified model allowed the calculation of the characteristic tunneling times of the process. A comparison is made between the results obtained in the model and the experimental data of Rhodobacter sphaeroides photosynthetic process.

Keywords: Quantum tunneling, electron transfer, photosynthesis, potential wells.

1. Introduction

Quantum tunneling, the problem of barrier penetration, is one of the most interesting and rich phenomena of quantum mechanics. Witnessing them are the multiple applications in quantum physics, from the most classic examples such as the ammonia molecule, α-decay in nuclear physics, the scanning microscope and many other effects in solid state physics, as in semiconductors, such as Esaki diode and the Josephson junction. Semiconductor devices such as diodes, transistors and integrated circuits can be found in everyday life, on televisions, cars, washing machines, diminished computers, quantum computers and so on. The tunneling phenomenon is also responsible for the high resolution field emission tunneling microscopy devices and manifests itself in complex theories of measurement fields through the known instantons, [1]. In biological systems quantum tunneling is centered on low temperature electron transport in proteins, [2]; see [3] for an overview.

For many decades the electron transfer has been the subject of much research, [4], [5]-[7]. Photosynthesis is one of the phenomena in which electron transfer is carried out with great efficiency, [8], occurring in plants, algae, bacteria and cyanobacteria. A process that has generated interest is the electron transfer in cytochrome c [9, 10].
In [11], DeVault and Chance suggested that a quantum treatment should be given to the electron transfer of this molecule. Then, experiments showed the temperature independence in electron transfer processes at low temperatures. In these experiments it can be observed that the charge transfer depends on the temperature up to a critical temperature value \( T_c \); for lower temperatures the transfer remains independent. This independence led to the conclusion that the electron transfer, under these conditions, occurs by electronic quantum tunneling [2].

In [12], using the Forster’s theory [13], Hopfield studied the electron transfer between two fixed sites under two conditions: high and low temperatures. The results were compared with previous results obtained on electron transfer in Chromatium and in Rhodopseudomonas sphaeroides bacteria; the distance dependence in the transference is discussed by a square barrier model.

Currently, studies of systems with high energy conversion efficiency, such as the photosynthetics, have been growing more and more, especially in photovoltaic cell research. One of the approaches used to study these processes involves the structure of multiple quantum wells, [14].

Many photosynthetic reaction centers are known, among them the reaction center of the purple bacterium Rhodobacter sphaeroides that is composed mainly by bacteriochlorophylls, pheophytins, quinones and cytochromes. In bacterial photosynthesis electron transfer occurs in cycles. The process starts with an infrared absorption which allows the electron excitation from the ground state to an excited state. Then, the electron is transferred by charge separation (donor-acceptor) to the cytochrome, which is the protein responsible for electron transport [15, 16]. At the end of the process the electron returns to its initial state, completing the cycle.

Inspired by all above information, this work proposes a temperature independent quantum mechanical model for the analysis of a photosynthetic system, based on a specific type of architecture of four asymmetric one-dimensional quantum square wells potential to analyse analytically the photoinduced electron tunneling in a cyclic system. The chosen approach aims at a determination of the energy eigenvalues by taking as a starting point the depth of the potential wells allied with a direction with which the electron is transferred along the wells. The transfer steps occur in pairs, from one well to its neighbor; the asymmetry helps to direct the electron transfers until it returns to the initial state. The energy eigenvalues for the proposed potential can be determined exactly by solving a sequence of asymmetric one-dimensional double well problem, each one characterized by a two level system, for which resonant states can be determined, [17]. The Rabi formula [18] can be applied to determine the tunneling times from one well to another. These times will be compared with the ones of the Rhodobacter sphaeroides purple bacteria.

This work is divided as follows: in Section 2 the cycle of bacterial photosynthesis is presented. In Section 3 the one-dimensional model of four asymmetric quantum square wells potential and the solution is described. Section 4 presents the quantitative results obtained for the eigenvalues and times of transfers. Section 5 contains the conclusions.
2. Bacterial Photosynthesis

As our interest focuses the bacterial photosynthesis, in particular the *Rhodobacter sphaeroides* purple bacteria, for which the photosynthetic reaction center is known, [15, 16], it is opportune a preliminary description of the biological process. Initially there is the absorption of a photon that causes the system to go from the ground state to an excited state. This initial energy is fundamental so that the electron begins to be transferred until returning to its initial state, in a cyclical process. The wavelength absorbed by the chlorophylls in this specific bacterium is 870nm. These chlorophylls that capture the photons are so essential for the photosynthesis that they are known as “special pair” and symbolized by the letter P. Then the excited electron decays successively passing by the bacteriochlorophylls (B), bacteriapheophytins (H), quinones (Q), and finally in the cytochrome that transports the electrons to the original state, closing the cycle. The bacteriapheophytins are very similar to the bacteriachlorophylls but do not have magnesium. Quinone is an oxidizing agent.

Two aspects of this process can be highlighted: the energy levels in which the electron is in each step of the transfer and the times involved in the transfers. In Table 1 it is possible to observe the values of these related parameters in each step of the electron transfer [15, 16].

| Step of the Transfer | $\Delta E$ (eV) | Time |
|----------------------|----------------|------|
| $P - H - Q \rightarrow ^*P - B - H - Q$ | 0 - 1.40 | |
| $^*P - B - H - Q \rightarrow P^+ - B^- - H - Q$ | 1.40 - 1.30 | 3ps |
| $P^+ - B^- - H - Q \rightarrow P^+ - B - H^+ - Q$ | 1.30 - 1.15 | 1ps |
| $P^+ - B - H^- - Q \rightarrow P^+ - H^- - Q$ | 1.15 - 0.65 | 200ps |
| $P^+ - H - Q^- \rightarrow P - H - Q$ | 0.65 - 0 | 100ms |

The initial excitation of the electron is clearly observed, resulting in a change in the energy level by the absorption of the photon. Next, we notice the decay of the energy levels and the return to the initial state at the end of the process. Figure 1(a) shows a scheme of the electron pathway through all stages of the transfer.

3. The one-dimensional model of four asymmetric square wells potential

Since *Rhodobacter sphaeroides* photosynthesis is performed in four main steps (transfers), the proposed model contains four asymmetric one-dimensional quantum square well potentials, as indicated in Figure(1b). The asymmetry of the wells, with different depths is a necessary feature to direct the electron transfer through all the steps of the cyclic process. The electron pathway in the model is simulated by an initial
absorption, then the electron tunnels and decays through the succession of barriers and wells until it returns to its initial state. The steps of the biological system are represented by arrows, shown in Figure 1(b). The parameters that need to be fixed are: the width ($a$) of the wells, the distance ($L$) between the center of one well to the center of the neighbour well and value of the potential barriers involved ($V$). All these parameters were fixed aiming for the existence of resonant states in the tunneling process, including for the return of the electron to the initial well (cyclic condition). The initial absorption with wavelength around $870 nm$ \cite{15, 16} is an essential constraint in the construction of the model, corresponding to a variation of the energy of $1.42 eV$.

The solution of the associated Schrödinger equation is analytically exact, thus allowing us to find the eigenfunctions and, with the appropriate boundary conditions, to determine the energy eigenvalues for each region of the potential. As the transfer occurs
in pairs of wells, from one well to its neighbor, the solution is obtained by breaking the potential in four sets of asymmetric double wells, where each double well is regarded as the junction of two single ones, and each well confined by an infinite barrier on one side and a finite barrier on the other side, [17]. Thus the physical problem to be solved involves an asymmetrical bistable well with respect to the depths \( V_0 \) and \( V_1 \) of the two wells involved, where \( V_0 < V_1 \), as shown in Figure 2. The transcendental equations obtained together with the wavefunctions for the two regions of interest are given in Table 2.

Because the wells are asymmetrical, the energy levels of a well relative to its neighbour may or may not match, depending on the depth of the potential. When the levels match these energy levels correspond to resonant states and the system can be approximated by a two-level system.

4. Results

After solving the transcendental equations of Table 2 with the constraints, the best value found for the width of the wells was \( a = 43.85 \AA \) and the distance \( L \) between the wells varies from 60 to 65\AA, as shown in Figure 3. These distances are compatible with the distances between the molecules at the photosynthetic reaction center of the bacterium studied [15], by considering that \( (L - a) \) is about 15\AA.

The condition that at the beginning of the process there is absorption of light (with energy of 1.42eV) imposes that the first well of the potential be deeper. Then the electron tunnels and then it decays, which suggests that the electron is transferred in a process of steps ensuring that it passes through all the desired levels.

To obtain the energy eigenvalues the model is solved in pairs, that is, \( V_1 \) with \( V_2 \),
Table 2. Wave functions and transcendental equations for the asymmetric one-dimensional double well [17], where \( L \) is the distance between the centers of the wells, \( a \) is the width of the wells, \( m \) is the electron mass, \( h = \frac{\hbar}{2\pi} \) where \( \hbar \) is Planck’s constant, \( V_0 \) and \( V_1 \) are the depths of the wells shown in Figure 2 and \( E \) is the energy eigenvalue to be determined graphically, with two possibilities: \( 0 < E < V_0 \) and \( V_0 < E < V_1 \).

| Energy: \( 0 < E < V_0 \) |
|----------------------------------|
| Parameters: \( k_1^2 = \frac{2m}{\hbar^2}((V_1 - V_0) - E), \beta^2 = \frac{2m}{\hbar^2}(V_1 - E), k_2^2 = \frac{2m}{\hbar^2}E \) |
| Wavefunctions: |
| Regions I and V: \( \Psi_I(x) = \Psi_V(x) = 0 \) |
| Region II: \( \Psi_{II}(x) = A_1e^{k_1x} + A_2e^{-k_1x} \) |
| Region III: \( \Psi_{III}(x) = Be^{\beta x} + Ce^{-\beta x} \) |
| Region IV: \( \Psi_{IV}(x) = D_1\sin(k_2x) + D_2\cos(k_2x) \) |
| Transcendental Equation: \( \frac{(k_1-\beta)e^{k_1(L-a)}+(k_1+\beta)e^{k_1(L+a)}}{((-k_1+\beta)e^{k_1(L+a)}-(k_1+\beta)e^{k_1(L-a)})} = \frac{(\beta-k_2\cot(k_2a))e^{-\beta(L-a)}}{\beta+k_2\cot(k_2a)} \)

| Energy: \( V_0 < E < V_1 \) |
|----------------------------------|
| Parameters: \( k_1^2 = \frac{2m}{\hbar^2}(E - (V_1 - V_0)), \beta^2 = \frac{2m}{\hbar^2}(V_1 - E), k_2^2 = \frac{2m}{\hbar^2}E \) |
| Wavefunctions: |
| Regions I and V: \( \Psi_I(x) = \Psi_V(x) = 0 \) |
| Region II: \( \Psi_{II}(x) = A_1\sin(k_1x) + A_2\cos(k_1x) \) |
| Region III: \( \Psi_{III}(x) = Be^{\beta x} + Ce^{-\beta x} \) |
| Region IV: \( \Psi_{IV}(x) = D_1\sin(k_2x) + D_2\cos(k_2x) \) |
| Transcendental Equation: \( \frac{(\beta+k_1\cot(k_1a))e^{\beta(L-a)}}{\beta-k_1\cot(k_1a)} = \frac{(\beta-k_2\cot(k_2a))e^{-\beta(L-a)}}{\beta+k_2\cot(k_2a)} \)

\( V_2 \) with \( V_3 \), \( V_3 \) with \( V_4 \) and \( V_4 \) with \( V_1 \), Figure 3.

In this way, solving numerically the transcendental equations for energy between \( 0 \) and \( V_0 \), \( (0 < E < V_0) \), and between \( V_0 \) and \( V_1 \), \( (V_0 < E < V_1) \), concerning the solution of the asymmetric double well shown in Table 2, it was found the first pair of wells with the deeper depth being \( V_1 = 1.585 eV \) and the other with the shallower depth, \( V_2 = 0.272 eV \). The model is then built in pairs and the junction of these pairs of wells is always done by repeating, in the next pair of wells, one of the values of the potential found. For the second pair of wells the potential \( V_2 \) was used as a constraint, finding then the third well, \( V_3 = 0.524 eV \) and also the fourth well, \( V_4 = 0.95 eV \) (Figure 3), always ensuring the constraints mentioned above. The energy eigenvalues are found graphically, as solutions of the transcendental equations.

Thus the cycle is the following: initially the electron in the ground state \( (E_0 = \)
0.01828\,eV) of the first well, $V_1$, is excited by a photon of wavelength 869.7\,nm to the resonant states 1.445\,eV and 1.460\,eV. The length of photon wave is obtained using the value of the energy absorbed, that is, 1.426676\,eV. Then, the electron tunnels to the second well, $V_2$, and decays to the ground state 1.329\,eV. This state is resonant with a state of the third well, $V_3$, which generates the resonant states of energy 1.329\,eV and 1.335\,eV allowing tunneling. Then the electron decays to the ground state of $V_3$ of energy 1.0785\,eV. Further tunneling occurs to the fourth well, $V_4$, with resonant states at 1.0785\,eV and 1.0787\,eV and the electron decays to the ground state of $V_4$ of energy 0.6529\,eV. The last tunneling occurs from $V_4$ to $V_1$ when the electron returns to the original state with the resonant energies of 0.6529\,eV and 0.6533\,eV. Finally, the electron tunnels to the initial well $V_1$ and decays to the ground state ($E_0 = 0.01828\,eV$), closing the cycle, as shown in Figure 3.

Figure 4 illustrates the intersection of the functions of the transcendental equation graph for energy within the two wells $V_1$ and $V_2$ with resonant states of energies 1.445\,eV and 1.460\,eV.

The resonance of states has an important relevance in this work, it reinforces the
Figure 4. Graphic of transcendental equation, Table 2 for $V_1 < E < V_2$, for energies given in joules. The intersections are at $E = 1.445eV = 2.31489.10^{-19}J$ and $E = 1.460eV = 2.33892.10^{-19}J$. Program used: Wolfram Mathematica.

The probability of electron tunneling through the potential barrier. This probability can be calculated by the formula of Rabbi, [18] presented in the following equation:

$$P_{12}(t) = \frac{4|W_{12}|^2}{(E_1 - E_2)^2 + 4|W_{12}|^2} \sin^2\left(\frac{(E_+ - E_-)t}{2\hbar}\right)$$  \hspace{1cm} (1)

where $W_{12}$ corresponds to the coupling between the wells involved in the tunneling, $E_1$ and $E_2$ are the original states corresponding to each individual single well and $E_+$ and $E_-$ represent the new eigenstates that result from the interaction between the wells.

In case the eigenvalues $E_1$ and $E_2$ are close enough (resonant) the term before the sine function is approximately one and the tunneling time ($T$) is obtained by considering the maximum value of the sine function, that is, its argument tends to $\frac{(2k+1)\pi}{2}$ for integer values of $k$. Thus

$$T = \frac{(2k+1)\pi\hbar}{E_+ - E_-}.$$  \hspace{1cm} (2)

Thus, using equation (2) with $k = 0$, the time for the electron to be transferred from the excited state ($1.460eV$) of well with depth $V_1$ to the ground state ($1.329eV$) of the well with depth $V_2$ is $T_1 = 0.14ps$. Following the same path, the electron is transferred to the well with depth $V_3$ with the time $T_2 = 0.4ps$ and with the time $T_3 = 33ps$ to the well with depth $V_4$. These times have an order of magnitude compatible to those obtained experimentally (Table 1).
The return time obtained experimentally is 100 ms, the longest time compared to the ones of the other stages of the transfer. This time can be understood through the suggested physical model, since the more distant the double wells are, the smaller the interaction between them and, consequently, the resonant states tend to the eigenvalue of the wells individually. Thus, if the variation between these energy levels \((E_+ - E_-)\) decreases, according to equation (2) the tunneling time increases.

In order for the process to be efficient it is necessary to compare the tunneling time with the electronic decay time. The decay time can be estimated through the Heisenberg Uncertainty Principle: \(\Delta E \cdot \Delta t = \frac{\hbar}{2}\) where \(\Delta E\) is the difference between the energy levels involved in the transition. The calculations however showed that the tunneling time dominates the process, with at least two orders of magnitude greater than the characteristic transition time.

5. Conclusions

Several biological processes, such as photosynthesis, involve electron transfer. In particular bacterial photosynthesis draws attention because it is a cyclic process.

In this work a photoinduced tunneling model composed by the structure of four asymmetric quantum square wells potential was suggested to simulate the electron transfer within the known reaction center of the purple bacteria *Rhodopseudomas sphaeroides*. The energy levels and the times required for the steps of the electron pathway were determined exactly. The basic conditions of the biological system were met, including the photon absorption of near 870 nm, the resonant states and the return to the ground state in 0.01828 eV (cyclic condition), Table 1.

The tunneling and electronic decay times were determined: the electron takes 0.14 ps to tunnel from the excited state from the first to the second well and decay to the ground state of this latter. Sequentially, the electron takes 0.4 ps and 3.3 ps to reach the ground state of the third and fourth well, respectively. The times obtained analytically by the model are lower than the times obtained experimentally, as seen in Table 1 [15, 16]. This discrepancy is attributed to the simplicity of the one-dimensional model studied which limits a quantitative adjustment in these times. Given its simplicity, the proposed model also allows qualitative understanding of the time it takes to the electron to return to the original state, being transferred from the fourth well to the first. Essentially, as the distance between the wells increases the tunneling time must also increase, equation (2). Quantitative results can be improved by increasing the number of physical parameters of the model. For instance, the individual width \((a)\) of each individual well can be varied. With such modifications it is expected that the model can be enriched, getting closer to the experimental results.

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