A quantum mechanical model for hole transport through DNA: predicting conditions for oscillatory/non-oscillatory behavior

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Abstract

A quantum mechanical model that considers tunneling and inelastic scattering has been applied to explain the hole transfer reaction from a G (Guanine) base to a GGG base cluster through a barrier of Adenine bases, (A)ₙ (n = 1-16). For n = 1, the ratio of tunneling to inelastic scattering is about 6, which is sharply decreased to around 0.23 and 5.23 × 10⁻⁸ for n = 4 and 16 respectively, suggesting dominance of inelastic scattering for n ≥ 4. As in experiment, the calculated product yield ratios (P₃GGG/P₃) exhibit a strong distance dependence for n < 4, and a weak distance dependence for n ≥ 4. We also predict conditions under which oscillatory or non-oscillatory charge transfer (CT) yield are expected.

Introduction

Charge transport (CT) through DNA is an important topic of recent interest and has biological significance as oxidation of a base forms a hole (positive charge) and initiates its transport from one base to a distant base, and hence, may result in mutations and carcinogenesis [1]. It is also important in the area of nanotechnology where researchers are trying to develop a highly conducting molecular wire with DNA [2-6]. Recently, it was shown theoretically that certain substituent groups attached to DNA bases can lower its activation energy barrier for hole transfer reaction, and hence, can enhance its conductivity [7]. Because of these potential applications in the field of molecular biology as well as materials science, significant amount of experimental [8-15] and theoretical studies [16-21] have been carried out on DNA and related systems [15] in order to understand the hole transport phenomenon. The experimental studies applied techniques like fluorescence quenching of the donor (as in ref.9) molecules, analysis of the strand cleavage products of DNA (as in ref.14), and cyclic voltammetry [15] for single and double stranded peptide nucleic acids. The experimental results are usually interpreted in terms of the following classical expression that relates the rate of CT (kₜ) to donor acceptor distance (R):

\[ kₜ = k₀ \exp (-βR) \]  

(1)

Here, \( k₀ \) is the pre-exponential factor, and \( β \) is the falloff parameter with a value ranging from around 0.1 to 1 Å⁻¹. While a large \( β \) value (close to 1) indicates a strong distance dependence of the CT rate, a small value indicates weak distance dependence. Grozema, et al. [17e] examined a correlation between the ionization energy (IE) difference between the donor and the bridge (barrier) and the \( β \) value, and have noticed that as the IE difference is increased the \( β \) value is also increased. For hole transfer from a G base to an acceptor through the intervening A bases (IE difference = 0.55 ev), this model predicts a fairly large \( β \) value of 0.85 Å⁻¹ (eq 1), and hence, suggests a tunneling mechanism. As the IE difference together with the \( β \) value gets significantly smaller, the charge is considered to become delocalized within the bridge and the mechanism is changed from the single-step tunneling to the molecular wire type. Thus, for a large \( β \) value and IE difference, as in G(A)ₙGGG system, only a strong distance dependence, and hence, tunneling is expected as a hole transfer mechanism. Giese, et al. [13], experiment, however, suggests a strong distance dependence followed by a weak distance dependence as n value is increased, even when the same IE difference is maintained between the donor and the bridge. In their experiment, the hole-water reaction...
who have proposed a similar change in tunneling for yield ratios (PGGG/PG) exhibit a strong distance dependence (Adenine-Thymine) base pair. The experimental product a GC (Guanine-Cytosine) base pair and A represents an AT for G(A)nGGG base sequence with products (P) are determined at different base sites for the yield, and hence, required additional studies.

O'Neill and Barton's [8] experiments suggest the weak distance dependence, the validity of hopping has been considered by quite a few researchers to address are oscillatory nature of CT yield [8] and charge delocalization [24], which have been observed in recent experiments. O'Neill and Barton's [8] experiments suggest an oscillatory CT yield with an increased number of A bases in Ap*(A)nG base sequence, where Ap* represents a photo-excited 2-aminopurine (Ap*) bonded to a T base. This result is quite different from that of Giese and co-workers where charge hops between base pairs until it reaches the acceptor. No matter whether a hopping or molecular-wire type transmission is considered for large n values, a change of mechanism from tunneling has been considered at n = 4. A recent molecular dynamics (MD) study [22] however, contradicts this suggestion of mechanism change at a particular n value (n = 4) as product formation was noticed within the A bases even for n = 2, at which coherent tunneling was considered to be the only mechanism. In order to account for their findings, the authors [22] assumed simultaneous operation of tunneling and hopping mechanisms. Although hopping has been considered by quite a few researchers to explain the weak distance dependence, the validity of hopping has been questioned on the basis of certain experimental results [23]. Similarly, the band-like hole transmission [10g] (molecular wire mechanism) is expected to give much larger product concentration within the A bases (barrier) than what has been observed in experiments [13].

Two other important aspects that any CT model needs to address are oscillatory nature of CT yield [8] and charge delocalization [24], which have been observed in recent experiments. O'Neill and Barton's [8] experiments suggest an oscillatory CT yield with an increased number of A bases in Ap*(A)nG base sequence, where Ap* represents a photo-excited 2-aminopurine (Ap*) bonded to a T base. This result is quite different from that of Giese and co-workers where the CT yield is non-oscillatory [13]. So far, no explanation has been provided for the oscillatory/non-oscillatory nature of CT yield, and hence, required additional studies.

A polaron model [21] incorporates some degree of charge delocalization and describes CT in terms of hopping between polaron sites. Although a drift of polarons (charge carrier) with accompanying polarization of the medium surrounding the DNA can explain the weak distance dependence for n > 3, it fails to account for strong distance dependence for n < 4 [23].

The research of various authors, discussed above, certainly indicates controversy rather than agreement on various DNA CT aspects. A number of questions can be raised regarding the CT phenomenon that we know today. What is the true nature of the CT mechanism; tunneling and hopping, tunneling and molecular wire-like transmission, or tunneling and altogether a different second mechanism? Also, do these mechanisms operate simultaneously at every n value or is there an onset of the second mechanism at n = 4? Besides, when would one expect oscillatory or non-oscillatory CT yield? In order to find answers to above questions the present theoretical study has been undertaken. Herein, we primarily focus on the issue of charge delocalization, CT mechanism and product formation at different base sites (in G(A), GGG structure) and the origin of oscillatory behavior that has been reported earlier [8]. This study is different from most other theoretical studies [16] in the sense that no change in CT mechanism is assumed a priori at any n value; rather, the hole transmission through the G(A)GGG base sequence is considered to be due to both tunneling and inelastic scattering that takes place simultaneously. It should be mentioned that the inelastic scattering is an expected phenomenon for a moving hole from its donor (G or Ap*) site to an acceptor site (GGG or G) through intervening A bases. This paper has been divided into several segments. First, we develop the CT mechanism, calculate product concentrations at different base sites, and at the end, provide conditions under which one can expect the oscillatory or non-oscillatory CT yield.

**Theory**

**Simplified 1D potential diagram for hole transportation**

The most common practice in electron transportation phenomenon in solid state physics is the consideration of effective mass approximation. In any periodic structure the effective mass approximation allows one to eliminate the periodic potential variation with distance and replace it by a flat potential profile. When one type of material forms a bond with another type, the energy profile for each type can be considered to be flat and a potential discontinuity is expected at the interface. In this theoretical study a DNA molecular chain is considered with a G base separated from a GGG base cluster by a number of A bases (1-16) that form an energy barrier as shown in figure 1. In this figure potential energy values on the far left and far right are assumed to be very large implying that there is no CT from the side chains. This assumption is quite consistent with the fact that each DNA base is bonded to the side chain via a deoxyribose sugar unit that has a large ionization potential (10.5 ev) [25].
However, the barrier on the immediate right side of the lone G site is finite (0.73 ev) [26] and is made up of A bases which the transporting hole from G to GGG will experience, and has been obtained from the calculated reorganization energy values [26]. While experiments do not provide a barrier height value for the hole transfer reaction, a significant fall in the CT rate with the number of intervening A bases suggests the presence of an energy barrier [13]. In addition, the reorganization energy values deduced from experimental rates [27] show an excellent agreement with the calculated values suggesting an accurately calculated reorganization energy values and hence, the value of the barrier height [26].

An overview of the quantum mechanical (QM) model

Before developing our QM CT model in details, we provide a physical picture of the model that involves the DNA structure of figure 1. As soon as a hole is formed on the G base (by loss of an electron) it remains confined within the base for a brief period of time. The wavefunction of this newly formed hole \( \psi_1 \) then gradually tunnels to GGG through the finite barrier width of \( (A)_n \) bases \( (n = 1, 2, 3, \text{ etc.}) \) and forms a distributed wavefunction \( \psi_2 \) throughout the potential structure of figure 1. Simultaneously, however, there takes place another phenomenon called “inelastic scattering” due to interaction of the hole with the vibrating atoms of the bases. Through such interaction the hole attains enough energy to move above the barrier, and hence, can flow directly from G to GGG. As the GGG interaction the hole attains enough energy to move above the barrier and the remote GGG base cluster, the solution will no longer remain as a time invariant one. A time dependent Schrodinger Equation is a complicated one to solve, for which we applied the following simple mathematical treatment after the consideration of three different hole states (initial, intermediate and final states, discussed in section 2.4). If any portion of the wavefunction interacts with the vibrating atoms of bases (referred to as inelastic scattering) and changes its original energy state, the probability of the existence of the hole in that particular state will gradually decrease. In order to include this effect, an imaginary quantity is introduced in the (E-V) term of equation (1a) to yield eqn (2).

\[
\frac{\partial^2 \psi}{\partial x^2} = \frac{2m}{\hbar^2} (E - V)\psi
\]  

(1a)

Here, \( m \) is the effective mass of the hole, \( \psi \) is its wavefunction for the energy state \( E \), and \( V \) is the potential energy. The above equation is a steady state equation when there is no change in particle energy, and under a bound condition of figure 1 potential there cannot be any probability current \( S \) in any direction. If we assume that after the formation of a hole at the lone G site its wavefunction interacts with the A bases in the barrier and the remote GGG base cluster, the solution will no longer remain as a time invariant one. A time dependent Schrodinger Equation is a complicated one to solve, for which we applied the following simple mathematical treatment after the consideration of three different hole states (initial, intermediate and final states, discussed in section 2.4). If any portion of the wavefunction interacts with the vibrating atoms of bases (referred to as inelastic scattering) and changes its original energy state, the probability of the existence of the hole in that particular state will gradually decrease. In order to include this effect, an imaginary quantity is introduced in the (E-V) term of equation (1a) to yield eqn (2).

\[
\frac{\partial^2 \psi}{\partial x^2} = \frac{2m}{\hbar^2} (E - V + iV_i)\psi
\]  

(2)

Here, \( i \) is the imaginary quantity and \( V_i \) is the newly introduced term in the equation. The \( V_i \) term can be treated either as a component of an imaginary energy or an imaginary potential. Whatever the choice is, the final equation remains the same. It may be noted that the imaginary potential term \( V_i \) is a function of temperature [28,29] as the molecular vibrations or even chemical reaction rates can vary with temperature. So, it is possible to address the temperature variation by making \( V_i \) as a function of temperature. For any given energy \( E \) of the hole, the functional forms of the wavefunction in different regions (Figure 1) are given below:

\[
\psi = Ce^{\gamma} + De^{-\gamma}
\]  

(3)

Where

\[ \gamma = \sqrt{2m_i (E + iV_i) / \hbar^2} \] for region PQ

\[ = \sqrt{2m_i (E - V + iV_i) / \hbar^2} \] for region QR

\[ = \sqrt{2m_i (E + iV_i) / \hbar^2} \] for region RS
Here \( V \) is the height of the potential barrier and \( m_1, m_2 \) and \( m_3 \) are the effective mass in PQ, QR and RS region (Figure 1) respectively. \( V_{im1} \) and \( V_{im2} \) are the imaginary potential in QR and RS regions respectively. Inelastic scattering in region PQ is ignored (\( V_{im1} = 0 \)). The usual solution technique of Schrodinger’s equation for such a potential structure involves application of boundary conditions at each potential discontinuity and evaluation of ‘C’s and ‘D’s for each region of a normalized wavefunction distribution. We used the technique presented in [30,31] to find out the eigenenergy and normalized wavefunction. The technique presented in [31] is particularly useful to evaluate normalized wave functions in presence of imaginary potentials. Once the wavefunction is known, the probability current density \( S \) (eqn.1b) can be easily calculated at any position using the form of solution presented in eqn.(3).

After the imaginary potential term is introduced within the A and GGG regions, the values of \( \gamma \) (eq.3) become complex resulting in gradual decay of the wave function in those regions due to inelastic scattering. If we represent the time constant of wave function decay as \( \tau_i \) then we can write

\[
\tau_i = \frac{\int \psi_i^2 \, dx}{S} \tag{4}
\]

Here, \( S \) is the probability current density at location \( Q \) (Figure 1) and has been defined by the number of holes being transferred per unit time. If such a process continues, after a while, the total wave function from the well at G will vanish and the hole will disappear from G and make a transition to GGG. No backward transition is considered as the initial metastable condition, and it is expected that the metastable wave function \( \psi_0 \) will tunnel through the barrier (Figure 1) and has been defined by the number of holes being transferred per unit time.

The potential energy diagram applied to calculate the hole state (Figure 1) for this state (\( \psi_0 \)) is SR0 then, the time constant \( \tau_1 \) for such a process to buildup \( \psi_1 \) is given by

\[
\tau_1 = \frac{\int_{GGG} \psi_0^2 \, dx}{S_{\psi_0}} \tag{5}
\]

If we assume that the probability of product formation rate at any location is directly proportional to the probability of hole existence (includes hole formation and decay) in that location and inversely proportional to the reaction time then

\[
P_{G0} = B \alpha_{G0} \tau_{CD} (1- \exp(-\tau_1 / \tau_{CD})) / \tau_{GC} \tag{6a}
\]

\[
P_{A0} = B \alpha_{A0} \tau_{CD} (1- \exp(-\tau_1 / \tau_{CD})) / \tau_{AC} \tag{6b}
\]

\[
P_{GGGo} = B \alpha_{GGGo} \tau_{CD} (1- \exp(-\tau_1 / \tau_{CD})) / \tau_{GGGC} \tag{6c}
\]

**Product formation during initial hole state**

As soon as a hole is formed at the G site, its wave function \( \psi_0 \) is primarily localized onto it with some penetration into the barrier on the right as shown in figure 2a. This is a metastable condition, and it is expected that the metastable wave function \( \psi_0 \) will tunnel through the barrier (Figure 2b) and elastically transform to the wave function \( \psi_1 \) (Figure 3), which the wave function is corresponding to the whole potential structure. The time required for such a transformation is the time required for the accumulation of wavefunction \( \psi_1 \) in GGG. If the probability current density at R (Figure 1) for this state \( \psi_0 \) is \( S_{\psi_0} \) then, the time constant \( \tau_1 \) for such a process to buildup \( \psi_1 \) in GGG is given by

**Figure 2:** (a) The eigenenergy and eigenfunction of the initial hole state at G when the hole is created. (b) The leakage of the wave function through the barrier after the creation of the hole.

**Figure 3:** The potential energy diagram applied to calculate the hole state after time \( \tau_1 \). The schematic wave function for the structure is shown as \( \Psi_1 \) corresponding to the energy \( E_1 \).
probability for product formation in state $\psi_0$. As deﬁned in eqns 6a
by $\psi_1$:

follows, similar to eqn. 6a, 6b and 6c, for the hole state deﬁned
in a similar manner. For a quick check of the formula 6a-

c and eqns in Appendix 1 for a detailed derivation). The
values of $\alpha$, deﬁned later in eqns 8 and 10, are also calculated
in a similar manner. A quantum mechanical model for hole transport through DNA: predicting conditions for oscillatory/non-oscillatory behavior

Here, $\tau_{XC}$ is the reaction time in the region $X$ (region for G, A or GGG in figure 1) and $\tau_{GC}$ is the mean reaction time for the entire structure (Figure 1) calculated by taking the weighted average of reaction rates (inverse of reaction time) in different regions (please see Appendix 1 for a detailed derivation). The proportionality constant $B$ takes into account any variation in the probability of existence of the wave function in the energy state under consideration and has the value of unity in this case as the hole is originated at this state. The $\alpha_{Xj}$ represents the probability of hole formation at a particular site and is calculated from the normalized wavefunction over the region $X$ by applying the following eqn:

$$\alpha_{Xj} = \int_{X} |\psi_{j}|^2 dx$$  \hspace{1cm} (6d)

Here, $X$ represents the region (G, A or GGG) and $j$ is the subscript for the wave function under consideration. If we consider $X$ to be the region for G and set $j = 0$, then eqn. 6d gives a value for $\alpha_{G0}$ obtained by integrating the square of the wave function $\psi_0$ over the region of G (PQ in figure 1). Other values of $\alpha$, defined later in eqns B and 10, are also calculated in a similar manner. A quantum mechanical model for hole transport through DNA: predicting conditions for oscillatory/non-oscillatory behavior

In addition to giving the total amounts of products at G, A or GGG sites (eqns 11-13), this model also allows one to calculate product values within any speciﬁc location by taking into account the wavefunction distribution at that location. For example, we can calculate the distribution of products within the individual G locations of the GGG cluster. If GGG(1), GGG(2) (middle G) and GGG(3) are the three G locations within the GGG cluster (region RS as shown in ﬁgure 1), then the amounts of products formed at these individual locations are proportional to the ratio of the probability at that location (G) to the probability at the region encompassing the GGG cluster corresponding to each of the wave functions, $\psi_0$, $\psi_1$ and $\psi_2$, and can be expressed as

$$\psi_0 = \frac{P_G}{P_{GGG}}$$

$$\psi_1 = \frac{P_A}{P_{GGG}}$$

$$\psi_2 = \frac{P_{GGG}}{P_{GGG}}$$

Product formation during intermediate hole state

As discussed above, soon after the hole is formed at the G site, its wave function changes from a nearly localized ($\psi_0$, Figure 2a) function to a delocalized function ($\psi_1$, Figure 3). Then, the wave function $\psi_1$ will decay gradually with a lifetime of $\tau_{2}$ where $\tau_2$ is calculated by eqn. 4.

Now, the product formation probabilities at G, A and GGG sites together with the total probability ($P_0$) are given as follows, similar to eqn. 6a, 6b and 6c, for the hole state deﬁned by $\psi_1$:

$$P_G = \left(1-P_0\right) \alpha_{G1} \tau_{C1} \left(1-\exp(-\tau_2/\tau_{C1})\right)/\tau_{GC}$$  \hspace{1cm} (8a)

$$P_A = \left(1-P_0\right) \alpha_{A1} \tau_{C1} \left(1-\exp(-\tau_3/\tau_{C1})\right)/\tau_{AC}$$  \hspace{1cm} (8b)

$$P_{GGG} = \left(1-P_0\right) \alpha_{GGG1} \tau_{C1} \left(1-\exp(-\tau_2/\tau_{C1})\right)/\tau_{GGGC}$$  \hspace{1cm} (8c)

As described earlier, $\alpha$ values are calculated by applying eq.6d with $j=1$ for different regions of bases. Here (1-$P_0$) = B, as defined in eqns 6a-c and eqns in Appendix 1, and $P_0$ is the probability for product formation in state $\psi_0$.

Product formation during final hole state and total quantities

As a result of inelastic scattering the hole ﬁnally makes a transition to the lowest energy state, $E_{GGG}$. Figure 4 shows the schematic potential energy diagram along with the probability distribution function for the final hole state represented by $\psi_2$. A quantum mechanical model for hole transport through DNA: predicting conditions for oscillatory/non-oscillatory behavior

Now, the product formation probabilities at G, A and GGG sites are given by following expressions, similar to eqns. 6a-c for the hole state deﬁned by $\psi_2$:

$$P_G = \left(1-P_0\right) \alpha_{G2} \tau_{C2} \left(1-\exp(-\tau_3/\tau_{C2})\right)/\tau_{GC}$$  \hspace{1cm} (10a)

$$P_A = \left(1-P_0\right) \alpha_{A2} \tau_{C2} \left(1-\exp(-\tau_3/\tau_{C2})\right)/\tau_{AC}$$  \hspace{1cm} (10b)

$$P_{GGG} = \left(1-P_0\right) \alpha_{GGG2} \tau_{C2} \left(1-\exp(-\tau_2/\tau_{C2})\right)/\tau_{GGGC}$$  \hspace{1cm} (10c)

This is the lower most state of the potential energy structure, and the backward transition to higher states by inelastic scattering has been ignored as the next higher state is about 0.5 eV higher than this lowest state, and has a very small probability of occupancy. Hence, the value of $\tau_2$ (time constant for hole transition to a higher state) is considered to be inﬁnitely large in eqns. 10a-c. As before, $\alpha$ values are obtained by using eqn. 6d with $j = 2$. Hence, the total probability for product formation at each base site is given by

$$P_G = P_{GGG} + P_G1 + P_{GGG2}$$  \hspace{1cm} (11)

$$P_A = P_{A1} + P_{A2} + P_{GGG}$$  \hspace{1cm} (12)

$$P_{GGG} = P_{GGG1} + P_{GGG2}$$  \hspace{1cm} (13)

In addition to giving the total amounts of products at G, A or GGG sites (eqns 11-13), this model also allows one to calculate product values within any speciﬁc location by taking into account the waveform distribution at that location. For example, we can calculate the distribution of products within the individual G locations of the GGG cluster. If GGG(1), GGG(2) (middle G) and GGG(3) are the three G locations within the GGG cluster (region RS as shown in ﬁgure 1), then the amounts of products formed at these individual locations are proportional to the ratio of the probability at that location (G) to the probability at the region encompassing the GGG cluster corresponding to each of the wave functions, $\psi_0$, $\psi_1$ and $\psi_2$, and can be expressed as

https://doi.org/10.29328/journal.jpra.1001022
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\[
P_{GGG}(r) = \sum_j P_{GGG}^{\alpha} (a_{GGG}(r)/a_{GGG})
\]

(14)

where \( j = 0, 1 \) or 2 (corresponding to the subscripts of the wave functions \( \psi_0, \psi_1 \) and \( \psi_2 \)) and \( a_{GGG} = \int_{GGG} |\psi_j|^2 \, dx \), where \( r \) is the G location within GGG (Figure 1) and assumes values 1, 2 or 3 and \( a_{GGG} = \int_{GGG} |\psi_j|^2 \, dx \). Since the calculation of \( \alpha \) requires \( \psi_0, \psi_1, \) and \( \psi_2 \) functions, in next section we discuss how to calculate these functions and their associated energies.

**Applying QM model for calculating \( \psi_0, \psi_1, \) and \( \psi_2 \)**

As mentioned above, these calculations were done numerically by using a method described in [30,31] and using the MATLAB series of programs [33]. In the calculation of \( \psi_0 \) we assume that soon after the formation of the hole at G, it will not experience the potential due to GGG, for which we consider a potential profile with an infinitely extended A barriers to the right as shown in figure 2a. With the barrier height [22] of 0.73 eV, the lowest eigenstate for the G well (Figure 2a) has the energy of 0.64 eV. Then, we assume a potential structure like that shown in figure 2b and calculated the rate of tunneling through the barrier of A bases. After tunneling, the wave function is distributed as shown schematically in figure 3, and is represented by \( \psi_x \). Since tunneling is a coherent process both \( \psi_0 \) and \( \psi_1 \) will have the same energy (0.64 eV). Although \( \psi_0 \) belongs to the lowest energy state for the potential structure of figure 2a, \( \psi_1 \) does not for the potential structure of figure 3 or 4. The lowest eigenstate \( (\psi_2) \) for the potential structure of figure 3 or 4 is substantially lower in energy with a value of 0.16 eV \( (E_{GGG}) \). For this large energy gap, the possibility of back transfer of hole from the low energy GGG site to high energy G site has been neglected in our numerical calculation. Even though for illustration purposes we provided schematic diagrams of wavefunctions (Figures 2-4), some of the actual functions, as calculated from the potential structure are presented later (Figure 7a-c).

We also examined other immediately higher energy states (which ranges from 0.565 to 0.612 eV) for different barrier widths, and find that they contribute very little toward the hole population or product concentration due to their lower probability of occupancy, and hence, these excited states were ignored. It is important to know that the hole populations at different eigenstates are determined by the Maxwell Boltzmann probability distribution function.

**Calculating current components for tunneling and inelastic scattering**

In calculating tunneling and scattered current components, we first assumed \( V = 0 \) in the barrier region (but not in GGG) so that there is no inelastic scattering due to the barrier, and all the current that is observed at the boundary of G and (A) \( n \) is due to tunneling current \( (S_T) \) only. Then, we introduced \( V \) in the barrier and calculated the current at G. This current includes both tunneling \( (S_T) \) and inelastically scattered \( (S_I) \) components. Thus, we separated the tunneling and scattered components from the total current and present results in table 1. Figure 5 shows how the ratio of tunneling to inelastic current density \( (S_T/S_I) \) decreases with an increased barrier width.

**Effective hole mass, imaginary potential and reaction time**

Because of the lack of reported results on effective mass or imaginary potential in the literature, we obtained these values by fitting the experimental data [13] points. These parameters were needed for the predictions of oscillatory and non-oscillatory nature of the product yield. The best fit curve and the data points are shown in figure 6. The effective masses of the hole at the G (or GGG) and A sites are determined to be around 1.42 \( m_0 \) and 1.50 \( m_0 \), respectively, where \( m_0 \) is the rest mass of an electron. These masses are in line with the typical hole masses that are considered in different charge transport phenomena in physics and electronic engineering. Similarly, the imaginary potential \( (\nu) \) value has been determined to be \( 0.25 \times 10^{-10} \) eV.

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**Table 1**: Tunneling and inelastic probability current components, \( S_T, S_I \), their ratio, and time involved in hole decay from the lone G (\( \tau \)) base are presented for different barrier widths \( (n = 1-16) \) of DNA base sequence, G(A)\( GGG \). The S values are in units of number of particles (holes)/sec and time constants are in seconds.

<table>
<thead>
<tr>
<th>n</th>
<th>( S_T )</th>
<th>( S_I )</th>
<th>( S_T/S_I )</th>
<th>( \tau (\text{sec}) )</th>
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<td>1</td>
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<td>6.0E+05</td>
<td>6.5E+00</td>
<td>5.6E-08</td>
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<td>2.4E-06</td>
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<td>1.6E-05</td>
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<td>1.6E-05</td>
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<td>1.2E-03</td>
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<td>3.1E+04</td>
<td>3.5E-04</td>
<td>1.6E-05</td>
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**Figure 5**: The tunneling \( (S_T) \)/inelastic scattering \( (S_I) \) ratios are presented against the number \( (n) \) of A barriers. The decrease in the ratio is most significant from \( n = 1-4 \), and then almost levels off. This result is obtained for the \( (G(A) GGG) \) sequence with a potential energy barrier [22] of 0.73 eV.
As discussed above, in the process of hole transfer from G to GGG, if the hole remains at a particular base site longer than the time required for its reaction with water, products will form. For the water trapping reaction with a hole at the G site (forming G+), the experiment by Giese and Spichy [34] provides a rate constant ($k$) value of around $6.0 \times 10^4$/s and hence, the time of reaction ($\tau_{GC}$) of $1.67 \times 10^{-5}$ sec ($1/k$). The same experiment also suggests reaction at the GGG site to be 3 times faster, and hence, $\tau_{GGG} = \tau_{GC}/3$. While the experiment suggests a much slower reaction at the A site, no rate constant value has yet been reported for the water trapping reaction at this site. In the absence of such experimental data, we examined a number of values by considering rate at A to be 5, 10 or 15 times slower than that at the G site. These results suggest that 10 times slower rate or $\tau_{AC} = \tau_{GC} \times 10$ gives a product concentration at A in better agreement with that of the experiment [13]. It is to be mentioned that only the percent product formation inside the barrier is dependent upon this value and has no effect on the overall findings of this study.

**Results and discussions**

**Nature of wave functions at different barrier widths**

Figures 7a-c are representative hole probability functions ($|\Psi|^2$) for $n = 1$ and $n = 6$ of G(A)$_n$GGG sequence obtained by applying the present QM model. The $\psi_2$ function is presented in figure 7a and $\psi_1$ and $\psi_2$ are presented in figure 7b and 7c. As the barrier width is increased from $n = 1$ (Figure 7b) to $n = 6$ (Figure 7c), a remarkable change in $\psi_1$ (dashed curve in 7b and 7c) function is noticed. As expected, for the smallest barrier width of $n = 1$, the wavefunction penetration within the barrier is significant suggesting relatively large hole concentrations at the A as well as GGG sites due to this wave function. For $n > 4$, the $\psi_1$ function (see dashed curve, Figure 7c for $n = 6$) exhibits a much decreased penetration resulting in a negligibly small hole concentration within the distant A bases of the barrier and the GGG site, and thus, reaches a probability distribution that remains almost unchanged for larger $n$ values (figures presented in supplemental information section).

The $\psi_2$ function (solid curve in 7b and 7c), on the other hand, shows large probability distributions at the G bases of the GGG cluster and much smaller probability distributions at the lone G base. Hence, $\psi_2$ is primarily responsible for hole concentration at the GGG destination site. As the $n$ value is increased from $n = 1$ to $n = 6$, the $\psi_2$ function shows increased confinement in GGG site suggesting its major contribution toward product formation for larger $n$ values. From the nature of these hole distribution functions it is obvious that the total hole concentrations at various base sites are given by the combined effect of $\psi_0$, $\psi_1$, and $\psi_2$ functions.

**Tunneling, inelastic scattering and CT mechanism**

Figure 5 shows how the probability ratio of tunneling ($S_T$) to scattering ($S_S$) decreases when the barrier width is increased from $n = 1-16$. Our calculations suggest that the actual transition from $\psi_0$ to $\psi_1$ is a fast process ($\tau_1$ varies from $1.5 \times 10^{-5}$ s for $n = 1$ to $1.2 \times 10^{-8}$ s for $n = 16$) for which practically, there is no contribution from $\psi_0$ towards the product formation. The major contribution of products comes from $\psi_1$ and $\psi_2$ states. The ratio of tunneling to inelastic scattering for $\psi_1$ is about 6 for $n = 1$ (one intervening A base), which decreases sharply as $n$ value is increased. Table 1 presents these values together with the time constant, $\tau_2$ (sec), for the decay of the wave function $\psi_1$ from the lone G base. While the tunneling current, $S_T$ (number of holes/sec), decreases consistently with the increased $n$ value, the inelastic scattering probability ($S_S$) initially decreases up to $n = 3$, then increases slightly and finally levels off at around $n = 5$. A possible explanation for
this trend can be due to the fact that the inelastic scattering is present both at A(n) as well as GGG sites. Eq.3 shows that the impact of imaginary potential will be stronger for smaller values of (E-V) or kinetic energy term while calculating the value of y. Physically, movement of the hole in A(n) region will be a slower process compared to its movement in GGG as kinetic energy in GGG region is much higher. Hence, the effect of inelastic scattering would be stronger in A(n) and weaker in GGG region. For smaller values of n significant inelastic scattering takes place in GGG compared to A(n) as A(n) is still very thin and contain a very small fraction of the total wavefunction (Figure 7b). As n increases, wave function in GGG decreases quite rapidly but increases in A(n) gradually. So, the interplay of these two inelastic scattering effects make the overall inelastic scattering decrease as n increases from 1 to 3. After that (n = 4 and 5) the wavefunction in GGG becomes very small to have any significant impact but fraction of wavefunction in A(n) keeps on increasing very slowly which is apparent from the increase value of Sj in table 1. For n > 5 the penetration of wavefunction inside A(n) saturates (Figure 7c) and the inelastic scattering does not show any further increase. Table 1 also shows that the decay time constant, τγ, increases with the increasing number of A bases until n = 4, and then remains constant. This result is consistent with the fact that a strong distance dependent CT takes place for n < 4 and a weak distance dependent CT takes place for n ≥ 4.

Product concentrations at different barrier widths

While hole concentrations at different base sites can be readily obtained from the probability wave functions (|ψ|^2), and are related to the amount of product formed, the exact calculation of product concentration requires hole reactivity at a base site and the survival time of the hole. With these considerations, and the application of equations 5-13, the product concentrations have been calculated. Table 2 presents percent product concentrations at different base sites for G(A)GGG system with n = 1-16. For the smallest barrier width of n = 1, a hole does not remain at the lone G or A site long enough to form any significant amount of products. Hence, the product concentration (P) is the largest at the GGG site (over 99%) and smallest at the lone G (0.27%) and A (0.15%) sites. As the barrier width is increased by adding another A base (n = 2), the hole finds it harder to get through the barrier, and hence, remains at the lone G and A sites for a longer amount of time. This results in larger product concentrations at the G and A sites of around 5% and 1%, respectively with the rest (94%) at the GGG site. This trend in concentration change is continued up to n = 4 when the product concentrations at the lone G, A and GGG sites are around 27%, 4% and 69% respectively.

Interestingly, for n > 4, the product concentrations at the base sites remain almost unchanged. At these barrier widths (n > 4), tunneling is insignificant (Table 1) compared to inelastic scattering, and hence, CT is primarily due to inelastic scattering, and hence, CT is primarily due to inelastic scattering of the hole, which almost levels off at n = 4. It should be pointed out that although the tunneling effect is quite small at n > 4, it consistently decreases and may explain a very small decreasing trend in productformation with increased n values. Although cannot be noticed within our reported number of decimal places in table 2, this decrease in product formation reflects a longer hole transportation time from G to GGG when the number of intervening bases (n value) is increased.

As mentioned earlier, our QM model gives product concentrations not only at the G, A and GGG sites it also predicts product concentrations at the individual base site of the GGG base cluster (Figure 1). For each n value, the product concentration, as calculated by using eq.14, is largest at the middle G (GGG(2), Table 2) and smallest at the farthest G (GGG(3), Table 2) of the GGG cluster, and is in agreement with the experimental results [13].

Hopping vs. other inelastic scattering mechanisms of CT

In our QM model, the imaginary potential incorporates a loss mechanism of the hole from any particular region. Hopping through the bridge is one such mechanism in which the hole acquires enough energy to overcome the barrier, and hence, leaves its original energy state to land onto the next state. In addition, there are other inelastic processes like chemical reactions that may also cause hole loss from a particular region. So, it is quite possible that more than one inelastic process may take place in a region. For example, within the bridge region the hole loss can be due to both hopping as well as chemical reactions. If the time constants for these individual processes are known, one would be able to estimate the extent of hopping through the bridge.

Origin of oscillatory/non-oscillatory CT yield

In order to examine the oscillatory CT yield in Barton’s experiment that involves Ap*(A)G sequence, and non-oscillatory CT yield in Giese’s experiment for G(A)GGG sequence, following calculations were carried out. First, we
calculated the energy barrier for the Ap(A)nG sequence by using the same procedure as was used for G(A)nGGG sequence [26]. In brief, reorganization energies (λ) were calculated by using the B3LYP/6-311++G** method [35-38] followed by the application of following Marcus’ eqn. (eqn. 15) [39]:

$$E_a = \frac{\lambda}{4} \left(1 + \frac{\Delta G}{\lambda}\right)^2$$  

These calculations yield a barrier height (E_a) of 0.19 ev, which is significantly smaller than that of G(A)nGGG system [26] with a barrier height of 0.73 ev. In eqn (15) ∆G is the free energy change for hole transfer from the donor to the acceptor.

In Giese’s system we obtained a bound state with an energy value of 0.64 ev, as discussed earlier, and is lower than the barrier height (0.73 ev) [26]. The same method, when applied to Barton’s system, did not result in any bound energy state suggesting that the energy of the hole for Ap*(A)nG system is larger than the barrier height (0.19 ev). These two distinct differences, E < V_o for Giese’s system, and E > V_o for Barton’s system provide incentive to apply QM transmission expressions (T, eqns 16 and 17) to see how the probability of hole transmission change in these two situations. Eqns 16 and 17 are well-known QM expressions derived for a rectangular barrier (like ours, without the potential wall on far left or far right of figure 1) with width a. For hole energy less than the barrier height, E < V_o, there is a non-zero transmission probability (tunneling) given by eqn 16, and is presented in figure 8a for different k1a (or a) values. In eqns 16 and 17, t is the amplitude of transmitted wave, T is the probability of transmission (or transmission coefficient), a is the barrier width, and k1 is a constant for a particular hole energy.

$$T = |t|^2 = \frac{1}{1 + V_o^2 \sinh^2(k_1a)} \frac{4E(V_o - E)}{4E(V_o - E)}$$  

$$k_1 = \sqrt{2m(V_o - E) / \hbar^2}$$

For energies greater than the barrier height, E > V_o, the T value is given by eqn 17 and is presented in figure 8b.

$$T = |t|^2 = \frac{1}{1 + \frac{V_o^2}{E-V_o}\sin^2(k_1a)} \frac{4E(V_o - E)}{4E(V_o - E)}$$  

$$k_1 = \sqrt{2m(E-V_o) / \hbar^2} \quad 0 < x < a$$

For eqn 16 we used V_o = 0.73 ev, E = 0.64 ev, and for eqn 17 we used V_o = 0.19 ev, and selected an E value larger than the barrier height with a value of 0.43 ev. Although 0.43 ev energy value has been selected arbitrarily, the value represents an approximate energy that is given off when a hole transfers from Ap+ to a G base involving ionization energy (IE) of G (to form G+) and electron affinity of Ap+ (-IE of Ap). The IE values were calculated by applying the B3LYP/6-311++G** method. Since figure 8a represents only the tunneling effect, there is no flat weak distance dependence segment of the curve as in figure 6. This confirms our finding that a second mechanism (inelastic scattering) must be present to account for the weak distance dependence of CT yield when E < V_o. The oscillatory nature of hole transmission is indeed observed for E > V_o (Figure 8b), which represents Barton’s experimental condition. Classically, the condition E > V_o would mean that the hole will be transferred from the donor to acceptor by simply passing over the barrier resulting in 100% transmission. However, in quantum mechanics, the incident wave from the donor side will suffer reflection at each of the potential discontinuities of the barrier even if E > V_o. Under such a condition, change in bridge length will change the phase of the forward and the reflected propagating waves and their interference give rise to the oscillations as observed in the transmission co-efficient shown in figure 8b. It is expected that the product formation at different base sites will be related to the hole transmission probability from a donor to the acceptor. It is interesting to note that the period of oscillation is around 3.0 (in K_a unit) in figure 8b, which corresponds to a barrier thickness (a) of 10.1 Å with 4 intervening A bases (10.1/3.4 + 1). For this calculation, first k_1 value (2.98 × 10^9 m^-1) was obtained assuming the mass of the hole to be close to (1.4 m_0) that obtained for a G or an A base in G(A)nGGG system (discussed earlier). The number of intervening A bases, thus obtained, is very close to that of the experiment with a value of around 3 (ref 8). Although the period of oscillation in figure 8b is close to that obtained in experiment, unlike the experiment,
the oscillatory function does not decrease with the increased barrier thickness (a). This is presumably the result of the simplicity of the transmission analysis in which back electron or hole (BET) transfer resulting from the hole reflection from the potential wall on the far right (Figure 1) has been ignored. In spite of this simplicity, the transmission analysis provides the origin of oscillatory/non-oscillatory patterns in CT yield and explains both Barton’s and Giese’s result. A more rigorous study is now underway to explain quantitatively the decreasing oscillatory function of the CT yield when the barrier width is increased.

**Comparison with density matrix theory**

May and Schreiber [40] in their density matrix theory (DMT) consider LUMOs (lowest unoccupied molecular orbitals) to be the localization centers for the extra electron from the donor. This extra electron moves within the pseudo-potential of the total electronic system of the entire molecule. In addition, the Hamiltonian, as defined in the DMT, also includes potential energy terms corresponding to contributions from environment (solvent) as well as molecular vibrations. For a large molecular system like G(A)GGG such calculations become very complicated. In our study much simpler treatment has been followed in which a hole moves within a rectangular potential barrier of A bases. Instead of LUMOs we considered bound states defined by a G base and the barrier due to A bases. Unlike DMT, the solvent effect has only been considered in an indirect manner through the use of an effective hole mass as well as the reaction rate (time constant) obtained by fitting the experimental data. Similarly, the effect of vibration on hole transfer has also been considered via the use of the imaginary potential.

**Concluding comments**

In our model simultaneous interplay of two mechanisms, tunneling and inelastic scattering, have been considered to explain the experimental results [13]. For $E < V_1$ (Giese’s experimental condition), the ratio of tunneling to inelastic scattering current decreases sharply from a value of around 6 for $n = 1$ to around 0.06 for $n = 5$. Without considering any mechanism change in advance for $n > 3$ or without explicitly considering hole hopping from one A to another, the model explains experimental results of product formations at different base sites. At every n value both tunneling and inelastic scattering takes place as the hole migrates from G to GGG. As in experiment, the present model explains a strong distance dependence of CT for $n = 1-3$ and a weak distance dependence for $n > 3$ (Figure 6). While most models consider the onset of a distance independent A-hopping mechanism for $n > 3$, our model predicts dominance of distance independent inelastic scattering ($S_e$) after an initial drop from $n = 1$ to $n = 3$ (Table 1). The weak to very weak distance dependence for $n > 3$ is due to a decreasing tunneling ($S_t$) probability superimposed on the inelastic scattering values. For $E > V_0$, an oscillatory function is obtained with a period of oscillation close to that obtained in the experiment.

**Acknowledgment**

The authors acknowledge helpful discussions with Joseph Genereux of Professor Barton’s group, and computation time provided on Linux machines by Numerically Intensive Computing Group at the center for Academic Computing at Penn State for some of the calculations.

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A quantum mechanical model for hole transport through DNA: predicting conditions for oscillatory/non-oscillatory behavior


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