Charge transfer via a two-strand superexchange bridge in DNA

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Charge transfer in a DNA duplex chain is studied by constructing a system with virtual electrodes connected to the ends of each DNA strand. The system is described by the tight-binding model and its transport is analyzed by the transfer matrix method. The very weak distance dependence in a long (G:C)(T:A)ₐ₋₉(G:C)₃ DNA chain observed in experiment [B. Giese, et al., Nature 412, 318 (2001)] is explained by a unistep two-strand superexchange bridge without the need for the multi-step thermally-induced hopping mechanism or the dephasing effect. The crossover number Mᵣ of the (T:A) base pairs, where crossover between the strong and weak distance dependence occurs, reflects the ratio of intra- and inter-strand neighboring base-base couplings.

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In recent years, charge migration in DNA has attracted considerable interest among the physics, chemistry, and biology communities. Charge transfer in DNA is important for functioning of molecular electronic devices ¹ as well as in understanding the DNA oxidative damage and repair ². Additionally, DNA offers a platform for fundamental physical understanding of systems in the nanoscale. It has been a long-standing problem to understand whether the charge transfer in DNA occurs via a unistep coherent superexchange process or a multi-step incoherent thermally-induced hopping process ³. In a one-strand unistep model the transfer rate is exponential and is strongly distance dependent ⁴ ⁵ ⁶. The multi-step hopping model on the other hand, predicts a weak dependence on the distance. Both of these ideas have received experimental supports ⁷ ⁸. Recent experiments have shown that the sequence of base-pairs may account for the transition between the strong and weak distance dependence of charge rates in DNA, but the underlying mechanism is not yet clear ⁹ ¹⁰. In Ref. ⁹, the transfer rate through a DNA of sequence (G:C)(T:A)₃₋₉(G:C)₃ was measured for different M. The charge transfer showed a strong distance dependence when M ≈ 3, but almost no distance dependence for M ≫ 3. To explain this distance-dependence crossover at M = 3, a combination of coherent superexchange and a hopping mechanism (incoherent) – the variable-range hopping model, was proposed to allow for a transition between these two regimes ⁷ ¹⁰. In the former process, the donor and the acceptor of the charge are coupled to the bridge of higher energy, without any chance of intermediate relaxation. The charge remains in a quantum state over the bridge that works as a tunneling barrier. In the hopping process, relaxation is introduced into each site and the charge loses its coherence (phase) when it reaches a site. A population parameter for each site was necessary to describe the distribution of the charge over the bridges.

In this letter, we demonstrate that the experimentally observed distance-dependence crossover can as well be explained by a simple two-strand superexchange model. The almost zero distance dependence of the charge transfer at a long chain is shown to be a result of the interstrand coupling in the DNA. In this model, the system still remains coherent and the charge transfer occurs in a unistep way.

We consider a DNA duplex chain of N Watson-Crick base pairs connected to four semi-infinite one-dimensional (1D) electrodes with one for each end of the first and the second strand as illustrated in Fig. ¹. The tight-binding Hamiltonian of the system is

\[ H = 2 \sum_{n=-\infty}^{\infty} [\varepsilon_n c_n^\dagger c_n - t_{n,n+1}(c_{n+1}^\dagger c_n + c_n^\dagger c_{n+1})] + 2 \sum_{n=-\infty}^{\infty} [u_n d_n^\dagger d_n - h_{n,n+1}(d_{n+1}^\dagger d_{n+1} + d_{n+1}^\dagger d_n)] - 2 \sum_{n=1}^{N} \lambda_n (c_n^\dagger d_n + d_n^\dagger c_n). \]

Here \( c_n^\dagger \) (\( d_n^\dagger \)) is the creation operator of holes in the first (second) strand on site n of the DNA chain (for \( 1 \leq n \leq N \)), the left electrodes (\( n \leq 0 \)), and the right electrodes (\( n \geq N + 1 \)). The on-site energy of site n in the first (second) strand is denoted by \( \varepsilon_n \) (\( u_n \)), which is equal to the highest occupied molecular orbit (HOMO) energy of the base on this site in the DNA chain and the center of conduction band in the electrodes. The coupling parameter of the first (second) strand \( t_{n,n+1} \) (\( h_{n,n+1} \)) is equal to the intra-strand coupling parameter \( t_d \) between neighboring sites n and \( n+1 \) of the DNA for \( 1 \leq n \leq N - 1 \), one-fourth of the conduction bandwidth in the electrodes \( t_m \) for \( n \leq -1 \) and \( n \geq N + 1 \), and the coupling strength \( t_{m,n} \) between the electrodes and the DNA strands for \( n = 0 \) and \( n = N \). The inter-strand coupling between sites in the same Watson-Crick base pair is described by \( \lambda_n \). The factor 2 multiplied to each sum in Eq. ¹ arises from the spin degeneracy.

In what follows, we have studied the intra-molecular hole transfer property along the DNA duplex chain after charges are injected (optically or electrically) into the base on site 1 of the first strand. To facilitate our calculation, we connect one virtual electrode to the left end of each DNA strand as the acceptor and another to the right end as the drain for holes. To minimize the contact effect, we assume a strong coupling (of coupling param-
eter $t_{01} = t_{N,N+1} = h_{01} = h_{N,N+1} = t_{dm} = 1.5 \text{ eV}$ between the electrodes and the sites at the ends of the DNA strands, and choose a band width ($4t_{dm}$) in the electrodes such that the optimal injection condition $t_d \times t_m = t_{dm}^2$ is satisfied. Our result is independent of the choice of the value of $t_{dm}$ once it is much larger than the coupling parameter between the sites inside the DNA. In this case, the added electrodes does not become a bottleneck of the system for the charge transfer and the calculated result predominantly reflects the properties of the DNA chain.

The transport properties are evaluated by the transfer matrix method \[11, 12\]. For an open system, the secular equation is expressed as a group of infinite number of equations of the form

$$
t_{n+1,n} \Psi_{n+1} + (\varepsilon_n - E) \Psi_n + \lambda_n \Phi_n + t_{n,n+1} \Psi_{n+1} = 0
$$

$$
h_{n-1,n} \Phi_{n-1} + (\varepsilon_n - E) \Phi_n + \lambda_n \Psi_n + h_{n+1,n} \Psi_{n+1} = 0
$$

with $\Psi_n$ ($\Phi_n$) the wave function of the first (second) strand on site $n$. The wave functions of the sites $n+1$ and $n$ are related to those of the sites $n$ and $n-1$ by a transfer matrix $M$,

$$
\begin{pmatrix}
\Psi_{n+1} \\
\Phi_{n+1}
\end{pmatrix}
= M
\begin{pmatrix}
\Psi_n \\
\Phi_n
\end{pmatrix},
$$

(1)

with

$$
M = \begin{bmatrix}
(E - \varepsilon_n) & -\lambda_n & t_{n,n+1} \\
\lambda_n & (E - \varepsilon_{n+1}) & -h_{n,n+1} \\
1 & 0 & 0
\end{bmatrix}.
$$

The transmission can be calculated by assuming the plane waves propagating in the electrodes. Here we are interested in the case where only holes are injected from electrode $L_1$ to the first strand. The hole wave functions in the $L_1$ electrode is $\Psi_n = (Ae^{ikL_1 \alpha} + Be^{-ikL_1 \alpha})$ ($n \leq 0$) and in the $R_1$ electrode $\Psi_n = Ce^{ikR_1 \alpha}$ ($n \geq N + 1$). The distance between two neighboring bases along any DNA strand is $a = 3.4 \text{ \AA}$. Using Eq. (1), we express the output wave amplitude $C$ in terms of the input wave amplitude $A$ and evaluate the transmission to $R_1$ electrode as

$$
T(E) = \frac{|C|^2 \sin(kLa)}{|A|^2 \sin(kLa)}.
$$

(2)

We have chosen the normalized incident amplitude to be $A = 1/\sqrt{\sin(kLa)}$.

To evaluate the transfer rate or current of a charge (hole) from the donor at the left-end site to the acceptor at the right-end site of the first strand, we need to know the chemical potential at each end. In the experiment of Ref. \[9\], a hole was injected to the left-end site. This means that the left chemical potential is approximately the on-site energy of this site while the right one is less. During the charge transfer process, the hole may retain the same energy if no inelastic scattering occurs or lose energy via the electron-phonon scattering or other inelastic collisions. Here we do not deal with these inelastic scattering mechanisms explicitly but analyze two limiting situations, between which the real charge transfer process occurs. Since our results for the distance dependence of the transfer rate from the two limits converge (see below), we conclude that our results are reliable.

In the first limit, we assume that there is no inelastic scattering involved and the hole energy is conserved during the transfer process. The transfer rate is proportional to the conductance of the system at equilibrium. For a small electric potential difference $k_BT/e$, the current is

$$
I = \frac{2e^2}{h} \int_{-\infty}^{\infty} dE T(E) [1 - f(E)] f(E).
$$

(3)

Here $f(E) = 1/\exp[(E - \mu)/k_BT]$ is the Fermi function. The room temperature $T = 300 \text{ K}$ is assumed and the on-site energy of site 1 in the first strand is used as the chemical potential $\mu$. In the second limit, we assume that the hole can lose energy freely during the process, and the transfer rate is proportional to the total current via all channels of energies below the hole's initial energy. This corresponds to an infinitely low chemical potential at the right electrode and the current is

$$
I = \frac{2e^2}{h} \int_{-\infty}^{\infty} dE T(E) f(E).
$$

(4)

We now calculate the distance dependence of the transfer rate using Eq. (2) and Eq. (3) in a DNA duplex, where the first strand has the base sequence G(T)$_M$GGG as in the experiment of Ref. \[3\]. The HOMO energies for bases G, C, T, A, are $E_G = 7.75$, $E_C = 8.87$, $E_T = 9.14$, and $E_A = 8.24 \text{ eV}$ respectively \[12\]. A uniform intra-strand hopping parameter $t_{n,n+1} = h_{n,n+1} = t_d$ ($1 \leq n \leq N - 1$) and a uniform inter-strand hopping parameter $\lambda_n = \lambda_d$ ($1 \leq n \leq N$) between any two neighboring bases in the DNA are used.
First we switch off the inter-strand coupling and calculate the dependence of the current $I$ on $\mathcal{M}$ as shown in Fig. 2(a), for different values of the intra-strand coupling parameter $t_d$. We find an exponential dependence of the current

$$I = I^M \propto e^{-\beta M a},$$

(4)

We then extract the values of $\beta$ for different $t_d$ and plot in Fig. 2(c) as $\beta$ versus $\ln(t_d)$ calculated via Eq. 3. The curves are almost linear, very similar to the results of Eq. (2), and converge to the approximate formula $[4, 5, 6]$.

$$\beta = \frac{2}{\alpha} \ln \frac{t_d}{E_T - E_G}.$$  

(5)

This is the well-known 1D superexchange result in the literature and has been derived in many different ways. This agreement confirms the validity of our model.

In the next step, we fix $t_d$ and switch on the inter-strand coupling by varying $\lambda_d$. The result is displayed in Fig. 2(b) where we choose $t_d = 0.5$ eV and plot $I$ versus $\mathcal{M}$ for a series of $\lambda_d$. Note that the charge transfer occurs via $\pi$-electrons and generally $\lambda_d < t_d$. For finite $\lambda_d$, the current drops exponentially with increasing $\mathcal{M}$ for small $\mathcal{M}$ and then becomes almost flat with oscillations around a limiting current $I^\infty$ for large $\mathcal{M}$. The crossover number $\mathcal{M}_c$ depends on the strength of the inter-strand coupling parameter. The weaker the inter-strand coupling is, the bigger the $\mathcal{M}_c$. The dependence of $I^\infty$ on $\lambda_d$ is approximately illustrated in Fig. 2(d), where the normalized current $I^{10}/I^1$ of the DNA chain at $\mathcal{M} = 10$ is plotted versus $\ln(\lambda_d)$. Again, two almost identical straight lines are found corresponding to the two limiting situations based on Eq. (2) and Eq. (3) and can be approximately expressed as

$$\ln(I^{10}/I^1) = 5.7 + 3.9 \ln(\lambda_d).$$

(6)

From Eqs. (4) - (3), we estimate the ratio of inter- and intra-strand coupling from the crossover number $\mathcal{M}_c$. Since the environment can change $\lambda_d/t_d$, we predict that the transition number may vary and be different from 3 when the experimental environment changes.

Calculating the current $I$ before and after adding a (T:A) base pair at site $n$ with zero or nonzero inter-strand coupling $\lambda_n$, we find that the distance-dependence crossover has a topological origin, viz., from the 1D chain network. When a new (T:A) base pair is inserted into the DNA chain, a new superexchange channel is opened through its inter-strand coupling and the corresponding contribution exactly compensates the loss of charge transfer rate that would incur because of an extra barrier to the existing channels.

In Fig. 3 we fit the $\mathcal{M}$ dependence of the charge transfer rate observed in Ref. 3 using intra- and inter-strand coupling parameters $t_d = 0.52$ eV and $\lambda_d = 0.07$ eV respectively. Eq. (4) is employed in the calculation. The agreement between the experimental and theoretical results are very good except that a small oscillation is visible in the theoretical result near $\mathcal{M}_c$. This oscillation results in the deviation of the empty circle from the filled circle at $\mathcal{M} = 4$. When $\mathcal{M}$ is used, similar result is obtained but with a stronger oscillation. The oscillations reflect the fact that we have treated the system as a coherent system by neglecting the dephasing effect from the environment and the relaxation process from phonons.

To get a clear picture of the process, we plot as inset in Fig. 3, the transmission $T$ as a function of the hole energy $E$ for systems with $\mathcal{M} = 1, 2, 3,$ and 7 in an energy range near and below the $G$ base HOMO energy $E_G$. In the $T$ spectrum, each peak represents a transport channel and there are more fine structures or peaks when more base pairs are added to the system. When $\mathcal{M}$ varies from 1 to 3, the 1D chain transport dominates and only one principal transmission peak is important. The principal peak shifts when $\mathcal{M}$ varies due to the shift of energy of the channel; its height drops rapidly leading to an exponential decrease of charge transfer rate. If we add more (T:A) base pairs to the DNA duplex, the principal peak drops to a level comparable to that of other peaks and results in a crossover from 1D chain transport to 2D network transport. In the absence of any inelastic scattering the charge transfer rate versus $\mathcal{M}$ oscillates as a result of the energy shift of the transport channels and the energy conservation of the charge. With the assistance of the phonon, however, the charge can use channels of energy.
The corresponding transmission between the (G:C) and the triple (G:C) base pairs. Inset: The role of inter-strand coupling between (G:C) base pairs versus energy $E$ for $M = 1$ (solid line), 2 (dotted line), 3 (dot-dashed line), and 7 (dashed line).

Our intra-strand coupling parameter $t_d = 0.52$ eV used to fit the measurement is consistent with the GG coupling parameter extracted from a direct I-V measurement through a DNA of 30 (G:C) base pairs [13]. This fit parameter is much larger than the ab initio values [12, 14]. The reason of this disagreement is not yet clear but it may be related to the electron-phonon interaction. This interaction may also affect the temperature dependence of the charge transfer through the system [15].

In summary, we propose a new mechanism for the charge transfer through a DNA duplex chain. It is different from the previously proposed thermally-induced hopping mechanism in explaining the observed weak distance dependence when the number of (T:A) base pairs between (G:C) base pairs is larger than $M_{tr}$, in that we treat the system fully quantum mechanically and emphasize the importance of inter-strand coupling between the two strands of the DNA duplex. We found that the series of (T:A) base pairs in long (G:C)(T:A)$_M$(G:C)$_n$ DNA duplex chains is still a quantum tunneling barrier. The holes in the left (G:C) base pair tunnel through this two-strand network superexchange barrier instead of one-strand chain superexchange barrier, to the right triple (G:C) base pairs.

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[1] E. Braun and K. Keren, Adv. Phys. 53, 441 (2004); C. Dekker and M.A. Ratner, Phys. World 14, (8), 29 (2001).
[2] K. Beckman and B.N. Ames, J. Biol. Chem. 272, 19633 (1997); S. Loft and H.E. Poulsen, J. Mol. Med. 74, 297 (1996); A.P. Grollman and M. Moriya, Trends in Genetics 9, 146 (1993).
[3] G.B. Schuster (Ed.), Long-range charge transfer in DNA, Springer-Verlag, Berlin Heidelberg (2004).
[4] H.M. McConnell, J. Chem. Phys. 35, 508 (1961).
[5] Y.A. Berlin, A.L. Burin, M.A. Ratner, Chemical Physics 275, 61 (2002); J. Jortner, M. Bixon, A.A. Voityuk, and N. Rösch, J. Phys. Chem. A 106, 7599 (2002).
[6] V. Mujica, A. Nitzan, Y. Mao, W. Davis, M. Kemp, A. Roitberg, and M.A. Ratner, in Electron transfer: from isolated molecules to biomolecules, Part Two, J. Jortner and M. Bixon, (Eds.), John Wiley & Sons, Inc., Page 403 (1999).
[7] S.O. Kelley and J.K. Barton, Science 283, 375 (1999).
[8] F.D. Lewis, X. Liu, J. Liu, S.E. Miller, R.T. Hayes, and M.R. Waslelewski, Nature, 406, 51 (2000); R.N. Barnett, C.L. Cleveland, A. Joy, U. Landman, and G.B. Schuster, Science 294, 567 (2001).
[9] B. Giese, J. Amaudrut, A. Köhler, M. Spormann, and S. Wessely, Nature 412, 318 (2001).
[10] T. Renger and R.A. Marcus, J. Phys. Chem. A 107, 8404 (2003).
[11] P. Carpena, P. Bernaola-galvan, P. Ch. Ivanov, and H.E. Stanley, Nature, 418, 955 (2002); H. Yamada, Int. J. Mod. Phys. B 18, 1697 (2004).
[12] E. Maciá, F. Tiozon, and S. Roche, Phys. Rev. B 71, 113106 (2005); S. Roche and E. Maciá, Mod. Phys. Lett. B 18, 847 (2004).
[13] D. Porath, A. Bezryadin, S. de Vries, and C. Dekker, Nature 403, 635 (2000).
[14] A.A. Voityuk, J. Jortner, M. Bixon, N. Rösch, J. Chem. Phys. 114, 5614 (2001).
[15] P.F. Barbara, T.J. Meyer, and M.A. Ratner, J. Phys. Chem. 100, 13148 (1996); R.A. Marcus, Rev. Mod. Phys. 65, 599 (1993); Z. G. Yu, Y. Song, Phys. Rev. Lett. 86, 6018 (2001).