

Transverse tunneling current through guanine traps in DNA

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The current-voltage dependence of the transverse tunneling current through the electron or hole traps in DNA is investigated. The hopping of the charge between the sites of the trap and the charge-phonon coupling results in a staircase structure of the I - V curve. For typical parameters of the DNA molecule, the energy characteristics of a DNA trap can be extracted from the I - V dependence, viz., for a small gate voltage the phonon frequency, and for a large gate voltage the hopping integral can be found from the positions of the steps in the I - V curve. Formation of the polaronic state also results in the redistribution of the tunneling current between the different sites of the traps.

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For the past several years intense research on electron (or hole) migration through DNA has established that these molecules are capable of transporting charges over a distance of at least a few nanometers.¹⁻⁴ This is primarily achieved by oxidation of guanines (G), which generates a guanine radical cation. Guanine has the lowest oxidation potential of the common DNA bases⁵ and therefore a guanine radical cation can only oxidize another G . Stacked G s such as GG , or a GGG , having much lower ionization potential than that of an isolated G , are known to act as *hole traps*.⁶ Since accumulation of holes at G sequences usually leads to deleterious effects, including mutations,^{2,7} charge migration through DNA may have important biological consequences. Electronic properties of both electron and hole traps depend crucially on the charge dynamics inside the trapping spots. Therefore, it is very important to extract the parameters that characterize such dynamics. Here we show how the energy characteristics of a DNA trap can be extracted from the current (I)-voltage (V) dependence of the transverse tunneling current through the electron or hole traps. Hopping of the charge between the sites of the trap and the charge-phonon coupling results in a staircase structure of the I - V curve. For a small gate voltage, the phonon frequency, and for a large gate voltage, the hopping integral, can be found from the positions of the steps in the I - V curve. Formation of the polaronic state also results in the redistribution of the tunneling current between the different sites of the traps.

Since our interest is in the local properties of DNA traps, transport in the direction perpendicular to the backbone axis (transverse transport⁸) is important. In this case, if the electrodes have a relatively small width, tunneling occurs through a single DNA nucleotide base. The saturated (unstructured) tunneling current then depends on the particular type of nucleotide base.⁸ This fact can be used to discover the sequence of DNA by scanning it with conducting probes. We demonstrate here that not only the saturated value of the tunneling current but also the *structure* of the I - V curves can provide important information on the properties of the DNA, in particular about the trapping spots. This is because the tunneling current through the system is determined by the density of states (DOS) of the system. For a finite system the

DOS has peaks corresponding to discrete energy levels. These peaks will result in a staircase structure of the tunneling current as a function of the applied voltage whenever the Fermi levels align with a new state of the system and thereby open an additional channel for tunneling. Therefore, from the staircase structure of the I - V curve, one can learn about the energy spectra of the system. For DNA, the trapping spots consist of a finite number of base pairs. Hopping between the base pairs within the traps determines the energy spectra of the spots. In addition to the energy scale due to hopping, there is also an energy scale due to the electron-phonon (or hole-phonon) interaction. Finally, for DNA trapping spots, the I - V dependence has two types of staircase structure: one due to hopping and the other due to the phonons. We have explored the interplay between these two effects.

The tunneling transport through a single molecule or a quantum dot with electron-phonon coupling has been extensively studied in the literature.⁹⁻¹² The main outcome of these works is the staircase structure of I - V curves due to phonon sidebands. The heights of the steps in this structure depend on the strength of the electron-phonon interactions, temperature, and on the equilibrium condition of the electron-phonon system. These studies were mainly restricted to a molecule with a single electron energy level, although a general approach to a many-level system is also formulated.¹¹

The DNA trap can be considered as a system of a few molecules (base pairs) with hopping between them and the electron-phonon coupling. Then in the I - V curves we should observe the interplay between the staircase structure due to hopping between the molecules and due to the phonon sidebands. Since the tunneling occurs only through a single base pair the I - V structure should also depend on the position of the base pair through which the tunneling current is measured. Here we consider only the hole traps and the tunneling current of holes, but the analysis is also valid for electron traps and electron transport. Whether it is a hole transport or electron transport depends on the gate potential, i.e., on the position of the chemical potential at zero source-drain voltage V_{sd} .

We disregard below the effects related to a Coulomb

blockade¹³ or to a double occupancy of the DNA traps, assuming that the repulsion between the holes is strong enough, although for some range of parameter of the traps the bipolaronic effect may become strong and a two-hole system can have lower energy than a single-hole system.¹⁴ For a single hole in the trap, the Hamiltonian of the trap and the electrodes consists of three parts: (i) the trap Hamiltonian, which includes a tight-binding hole part with hopping between the nearest base pairs—the Holstein’s phonon Hamiltonian with diagonal hole-phonon interaction,¹⁵ (ii) the Hamiltonian of two leads, left (L) and right (R), and (iii) the Hamiltonian corresponding to tunneling between the leads and DNA traps

$$\mathcal{H} = \mathcal{H}_{\text{trap}} + \mathcal{H}_{\text{leads}} + \mathcal{H}_t, \quad (1)$$

where

$$\begin{aligned} \mathcal{H}_{\text{trap}} = & \sum_{i=1}^{N_t} \epsilon a_i^\dagger a_i - t \sum_i [a_i^\dagger a_{i+1} + \text{h.c.}] \\ & + \hbar\omega \sum_i b_i^\dagger b_i + \chi \sum_i a_i^\dagger a_i (b_i^\dagger + b_i), \end{aligned} \quad (2)$$

$$\mathcal{H}_{\text{leads}} = \sum_{k,\alpha=L,R} \epsilon_k d_{\alpha,k}^\dagger d_{\alpha,k}, \quad (3)$$

$$\mathcal{H}_t = -t_0 \sum_{\alpha=L,R,k} [a_{i_0}^\dagger d_{\alpha,k} + \text{h.c.}], \quad (4)$$

where a_i is the annihilation operator of the hole on site (base pair) i , ϵ is the on-site energy of the hole in the trap (the same for all base pairs within the trap and determined by the gate voltage or doping of DNA), b_i is the annihilation operator of a phonon on site i , t is the hopping integral between the nearest base pairs, ω is the phonon frequency, χ is hole-phonon coupling constant, and $d_{\alpha,k}$ is the annihilation operator of a hole in the lead $\alpha=L,R$ with momentum k . The index $i=1, \dots, N_t$ in Eq. (2) labels the sites (base pairs) in the trap and N_t is their total number. Tunneling from the leads to the trap occurs only to the site i_0 with the tunneling amplitude t_0 . In the hole-phonon part of the DNA Hamiltonian $\mathcal{H}_{\text{trap}}$, we include only the optical phonons¹⁶ with diagonal hole-phonon interaction.

We describe the process of tunneling through the trap as a sequential tunneling.¹⁷ In the weak lead-trap coupling regime the tunneling Hamiltonian \mathcal{H}_t can be considered as a perturbation that introduce the transitions between the states of the trap Hamiltonian, $\mathcal{H}_{\text{trap}}$. We denote the eigenstates of the trap Hamiltonian without coupling to the leads as $|0, m\rangle$ with energy $E_{0,m}$ for the trap without any holes, and $|1, n\rangle$ with the energy $E_{1,n}$ for trap with a single hole. In the weak lead-trap coupling limit the master equation for the density matrix of the trap reduces to the rate equation¹⁰ for probability $P_{0,m}$ to occupy the state $|0, m\rangle$ and probability $P_{1,n}$ to occupy the state $|1, n\rangle$,

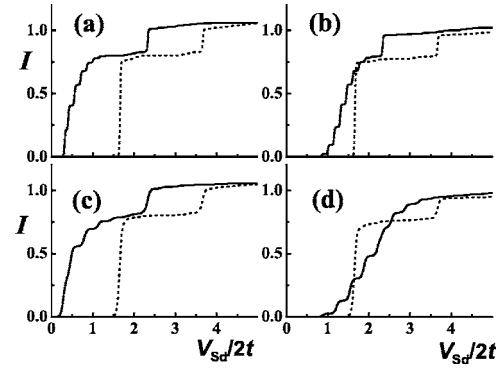


FIG. 1. Current vs the source-drain voltage shown for two base pairs in the trap ($N_t=2$) and different values of phonon frequency and hole-phonon interaction strength: (a) $\gamma=0.1$, $\lambda=0.5$; (b) $\gamma=0.1$, $\lambda=1.0$; (c) $\gamma=0.2$, $\lambda=0.5$; (d) $\gamma=0.2$, $\lambda=1.0$. The solid line corresponds to $\epsilon=1.3t$ while the dotted line is for $\epsilon=2.7t$.

$$\begin{aligned} \frac{dP_{1,n}}{dt} = & \sum_{m,\alpha=L,R} W_{\alpha,mn}^{0 \rightarrow 1} P_{0,m} - \sum_{m,\alpha=L,R} W_{\alpha,nm}^{1 \rightarrow 0} P_{1,n} \\ & - \frac{1}{\tau} \left[P_{1,n} - P_{1,n}^{eq} \sum_{n'} P_{1,n'} \right], \end{aligned} \quad (5)$$

$$\begin{aligned} \frac{dP_{0,m}}{dt} = & \sum_{n,\alpha=L,R} W_{\alpha,nm}^{1 \rightarrow 0} P_{1,n} - \sum_{n,\alpha=L,R} W_{\alpha,mn}^{0 \rightarrow 1} P_{0,m} \\ & - \frac{1}{\tau} \left[P_{0,m} - P_{0,m}^{eq} \sum_{m'} P_{0,m'} \right]. \end{aligned} \quad (6)$$

The distributions $P_{1,n}^{eq}$ and $P_{0,m}^{eq}$ are the corresponding equilibrium distributions with temperature T , $P_{1,n}^{eq} = \exp(-E_{1,n}/k_B T) / \sum_{n'} \exp(-E_{1,n'}/k_B T)$ and $P_{0,m}^{eq} = \exp(-E_{0,m}/k_B T) / \sum_{m'} \exp(-E_{0,m'}/k_B T)$. Here τ is the relaxation time that is assumed to be same with and without a hole in the trap. The transition rate $W_{\alpha,nm}^{1 \rightarrow 0}$ is the rate of hole tunneling from the state $|1, n\rangle$ of the trap to the $\alpha=L,R$ lead leaving the trap in the state $|0, m\rangle$. Similarly, the rate $W_{\alpha,mn}^{0 \rightarrow 1}$ is the rate of hole tunneling from the lead α to the state $|1, n\rangle$ of the trap, while originally the trap was in the state $|0, m\rangle$. These rates can be found from Fermi’s golden rule

$$W_{\alpha,nm}^{1 \rightarrow 0} = \Gamma_0 f_\alpha(E_{1,n} - E_{0,m}) |\langle 0, m | a_{i_0} | 1, n \rangle|^2, \quad (7)$$

$$W_{\alpha,mn}^{0 \rightarrow 1} = \Gamma_0 [1 - f_\alpha(E_{1,n} - E_{0,m})] |\langle 0, m | a_{i_0} | 1, n \rangle|^2, \quad (8)$$

where $\Gamma_0 = 2\pi t_0 \rho / \hbar$ and ρ is the density of states in the leads, which is assumed to be the same in the L and R leads, and $f_\alpha(\epsilon)$ is the Fermi function of the lead α with a chemical potential μ_α .

For the stationary case the time derivatives of $P_{1,n}$ and $P_{0,m}$ are zero, and Eqs. (5) and (6) becomes the system of linear equations with condition of normalization $\sum_n P_{1,n} + \sum_m P_{0,m} = 1$. Then the stationary current can be calculated as

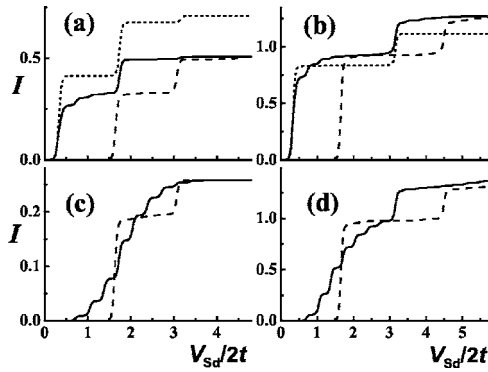


FIG. 2. Current vs the source-drain voltage shown for three base pairs in the trap ($N_t=3$) and $\gamma=0.2$, but for different tunneling points i_0 and different values of hole-phonon interaction strength: (a) $i_0=1$: $\lambda=0.5$ and $\epsilon=1.7t$ (solid), $\epsilon=3.0t$ (dashed), $\lambda=0$ and $\epsilon=1.7t$ (dotted); (b) $i_0=2$: $\lambda=0.5$ and $\epsilon=1.7t$ (solid), $\epsilon=3.0t$ (dashed), and $\lambda=0$, $\epsilon=1.7t$ (dotted); (c) $i_0=1$: $\lambda=1$ and $\epsilon=1.7t$ (solid), $\epsilon=3.0t$ (dashed), (d) $i_0=2$: $\lambda=1$ and $\epsilon=1.7t$ (solid), $\epsilon=3.0t$ (dashed).

$$I = \sum_{n,m} [P_{0,m} W_{L,mm}^{0 \rightarrow 1} - P_{1,n} W_{L,nn}^{1 \rightarrow 0}]. \quad (9)$$

We have calculated the current (9) numerically as a function of V_{sd} for different values of on-site energy, ϵ , which can be changed by the gate voltage or by doping. By varying V_{sd} we are keeping the on-site energy ϵ the same and vary the chemical potentials of leads as $\mu_L = V_{sd}/2$ and $\mu_R = -V_{sd}/2$.

To determine the tunneling current we first calculate the energy spectra of the DNA Hamiltonian [Eq. (2)] without holes and with a single hole in the trap. The H_{trap} then is just the Hamiltonian of free phonons at each site of the trap. With a single hole we make the system finite by introducing limitations on the total number of phonons¹⁸ $\sum_i n_{\text{ph},i} \leq 10$, where $n_{\text{ph},i}$ is the number of phonons on site i . The eigenfunctions and eigenvalues of $\mathcal{H}_{\text{trap}}$ can then be found numerically and the corresponding transition rates Eqs. (7) and (8) can be calculated. Finally, we solve the system of linear Eqs. (5) and (6) for a given bias voltage, and substitute this solution into Eq. (9) to find the stationary tunneling current.

There are five dimensionless parameters that determine the tunneling current I at a given temperature: the nonadiabaticity parameter¹⁹ $\gamma = \hbar\omega/t$, with a typical value of $\sim 0.01-0.5$ for DNA,²⁰ the canonical hole-phonon coupling constant¹⁹ $\lambda = \chi^2/(2\hbar\omega t)$, which is $\sim 0.2-1$ for DNA,²¹ dimensionless bias voltage V_{sd}/t , on-site energy ϵ/t , and the ratio of the relaxation time and the tunneling time $\tau\Gamma_0$.

The calculations have been performed for $N_t=2$ and $N_t=3$, i.e., for two and three base pairs in the trap. The example of such a system could be the guanine hole traps: *GG* and *GGG* spots surrounded by adenines. In all the calculations we kept the ratio of relaxation and tunneling time equal to 1 ($\tau\Gamma_0=1$), i.e., the hole-phonon system in the trap is not in the equilibrium. Different values of $\tau\Gamma_0$, ranging from $\tau\Gamma_0 \ll 1$ (equilibrium case) to $\tau\Gamma_0 \gg 1$ (disequilibrium case) do not modify qualitatively the behavior of the I - V curve. To detect the phonon steps in the I - V curve the temperature should be

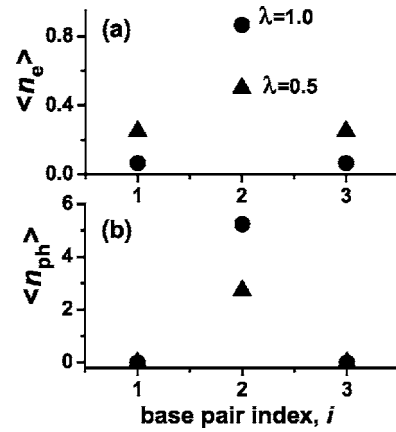


FIG. 3. (a) The average number of holes and (b) the average number of phonons for a single hole system in a *GGG* trap are shown as a function of the base index. Dots and triangles corresponds to hole-phonon interaction strength $\lambda=1.0$ and 0.5 eV, respectively.

less than the phonon frequency and so we keep the temperature equal to $0.01t$, which for $t=0.1$ eV is around 10 K.

In Fig. 1 our results are shown for two base pairs (sites) in the trap. The tunneling occurs through one of the sites, $i_0=1$. For the uncoupled hole-phonon system the I - V dependence has two steps corresponding to two single hole energy levels. The distance between the steps is $\delta V_{sd}=4t$. For a small hole-phonon coupling constant $\lambda=0.5$ [Figs. 1(a) and 1(c)] the additional structures of width $\delta V_{sd} \approx \hbar\omega$ due to the phonon sidebands appear only at the first step and the second step can still be clearly distinguished. At the same time for a large gate voltage (large on-site energy ϵ), the phonon steps are suppressed and the I - V structure becomes similar to that of a zero-coupling strength, which is shown in Figs. 1(a) and 1(c) by dotted lines. For a strong hole-phonon interaction ($\lambda=1$) the phonon steps suppress the steps due to intersite hopping within the trap [Figs. 1(b) and 1(d)]. This suppression becomes stronger for a larger nonadiabaticity γ , which is illustrated in Figs. 1(b) and 1(d) by a solid line for $\gamma=0.1$ and $\gamma=0.2$. With increasing gate voltage the phonon steps disappear and the I - V curve shows a clear two-step structure. The suppression of phonon steps is not an artifact of specific choice of the parameter $\tau\Gamma_0$. We have found that this effect exists for all values of the relaxation time. The origin of the suppression can be much easier to understand in the regime of a very fast relaxation. Hence we explain the suppression of phonon steps in the case when the relaxation time is much shorter than the tunneling time. In this case, the hole-phonon system will be in equilibrium before each step of tunneling process occurs. At low temperatures this means that the system will be at its ground state, i.e., without any phonons if there are no holes in the trap or in the polaronic state when there is a single hole. Then tunneling from the L lead will be tunneling to the state without any phonons. Therefore this process will probe only single hole states, which results in a two-step structure due to hole hopping. Tunneling to the R lead is from the ground state of the coupled hole-phonon system and so this tunneling will result in the phonon steps in the I - V dependence. With increasing

gate voltage or on-site energy the number of channels contributing to the tunneling to the R lead is increased. Finally at large enough gate voltage this tunneling current becomes saturated with suppression of phonon steps in the I - V structure. From Fig. 1 we conclude that for typical parameters of the DNA structure, the hopping integral between the sites within the DNA traps and phonon frequency that determine the energetics of the hole-phonon trap system, can be found from dependence of the tunneling current on V_{sd} . From a small gate voltage the phonon frequency can be found from the I - V curve, while for a larger gate voltage the hopping integral can be obtained.

The I - V curve should show even richer structures for a larger number of sites in the trap. In Fig. 2 the current as a function of bias voltage is shown for $N_t=3$ sites. In this case tunneling is possible through the sites $i_0=1$ and $i_0=2$. For uncoupled hole-phonon systems the I - V curve shows three steps for $i_0=1$ [dotted line in Fig. 2(a)], and two steps for $i_0=2$ [dotted line in Fig. 2(b)]. This means that for $i_0=2$ only two states have nonzero amplitude at $i=2$ and contribute to the tunneling current. The finite hole-phonon coupling results in two effects: the phonon steps in the I - V dependence similar to two-site trap (Fig. 1), and the polaronic effect that redistributes the hole density along the trap and increases or decreases the tunneling current.

For small hole-phonon coupling ($\lambda=0.5$) the phonon steps

are seen only at the first hopping step [Figs. 2(a) and 2(b) (solid lines)]. The separation between the steps is the phonon frequency. Similar to Fig. 1, an increase of the gate voltage (on-site energy) suppresses the phonon steps and the I - V curve becomes similar in structure to the uncoupled case [Figs. 2(a) and 2(b) (dashed lines)]. For a larger hole-phonon coupling ($\lambda=1$) the steps due to hole hopping almost completely disappear for $i_0=1$ [Fig. 2(c), solid line], but some structure is still visible for $i_0=2$ [Fig. 2(d), solid line]. For a larger gate voltage the steps due to the hopping overcome the phonon effects.

The polaronic effects due to hole-phonon coupling can be clearly seen in Fig. 2. With increasing hole-phonon interaction the hole states become more localized at the center of the trap (see Fig. 3), which results in an increase of the current for tunneling through the central site of the trap $i_0=2$ [see Figs. 2(b) and 2(d)], and decrease of the current through $i_0=1$ [see Figs. 2(a) and 2(c)]. In addition to changes to the tunneling current, the polaronic effect also modifies the structure of the I - V curve. This can be seen in Fig. 2(a), where with increasing hole-phonon interaction the third step due to the hole hopping disappears.

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