Electric Conduction in Short DNA Wires

Weihua Mu\textsuperscript{1,}\textsuperscript{*} and Zhong-can Ou-Yang\textsuperscript{1,2}

\textsuperscript{1}Institute of Theoretical Physics, The Chinese Academy of Sciences, P.O.Box 2735 Beijing 100080, China
\textsuperscript{2}Center for Advanced Study, Tsinghua University, Beijing 100084, China

Abstract

A strict method is used to calculate the current-voltage characteristics of a double-stranded DNA. A more reliable model considering the electrostatic potential drop along an individual DNA molecular wire between the contacts is considered and the corresponding Green’s Function is obtained analytically using Generating Function method, which avoids difficult numerical evaluations. The obtained results indicate that the electrostatic drop along the wire always increases the conductor beyond the threshold than without considering it, which is in agreement with recent experiments. The present method can also be used to calculate the current-voltage characteristics for other molecular wires of arbitrary length.

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Recently, the progress of molecular wires attracts much attention on their transport behaviors. A number of experimental groups have reported measurements of the current-voltage (I-V) characteristics of molecules, especially Deoxyribonucleic Acid (DNA). DNA has a special double-helix structure with complementary nucleotide base-pairs stacking onto each other, which could possibly be a candidate for one-dimensional electronic transport. Intense experimental investigations have already been made on the transport properties of DNA. Using scanning tunneling microscope technique, Dunlap et al. found that DNA is an insulator. Fink and Schoenenberger measured I-V characteristics of λ-DNA ropes consisting of a few double-stranded DNA (dsDNA) molecules by low energy electron bombardment technique, and found a linear current-voltage relation. Kasumov et al. measured small number of DNA molecules, and observed proximity-induced superconductivity. In particular, Porath et al. directly measured electrical transport through individual DNA molecules, and suggested DNA to be a semiconductor with a voltage gap. To explain experimental disputes, several theoretical models ranging from the Hückel model to the density functional theory have been developed.

In the present paper, we investigate theoretically Porath’s experiment and calculate the current between two electrodes which are connected by a DNA molecular wire. To use a simple model illustrating the basic physics, we follow the algorithm proposed by Mujica. The model Hamiltonian can be written as the sum of two terms,

\[ H = H^0 + H', \]

where \( H^0 \) is the non-interacting Hamiltonian for the electrodes (electron reservoirs) and DNA molecule, and \( H' \) represents the coupling of contacts and DNA molecule. Using extended Hückel model, \( H^0 \) and \( H' \) can be expressed as

\[ H^0 = \sum_i E_i^0 |i\rangle\langle i| + \sum_{\alpha=1}^N E_\alpha^0 |\alpha\rangle\langle \alpha| + \sum_f E_f^0 |f\rangle\langle f| + \sum_{\alpha=1}^{N-1} \beta |\alpha\rangle\langle \alpha+1| + h.c. \]

(2)

\[ H' = \sum_i V_{i1} |i\rangle\langle 1| + \sum_f V_{Nf} |N\rangle\langle f| + h.c., \]

(3)

where the sum on \( |i\rangle \) (\( |f\rangle \)) runs over the state in the continuum of left (right) reservoirs. A DNA molecular wire consists of \( N \) sites, with one state per site, which is denoted by \( |\alpha\rangle \).
$V_{1i}$ ($V_{Nf}$) is the tunneling parameter from the left (right) reservoir to the single electron state 1($N$) in the molecule. T-matrix formalism of scattering theory [13] gives differential conductance [10]:

$$g = \frac{2e^2}{\pi \hbar} |G_{1N}|^2 \Delta_A(E_f) \Delta_B(E_f),$$  

(4)

where $G_{1N}$ is the (1$N$) element of the matrix formula Green’s Function $G$, it is related to the molecule’s site 1 and $N$. $\Delta_1$ and $\Delta_N$ are semielliptical reservoir spectral densities defined through Newns’ chemisorption theory [14]:

$$\Delta_K(E) = \begin{cases} \frac{V_{K}^2}{\gamma} \sqrt{1 - (E/2\gamma)^2}, & |E/2\gamma| < 1, \\ 0, & |E/2\gamma| > 1, \end{cases}$$  

(5)

where $E$ is measured from the center of reservoir energy band caused by chemisorption in the surface of the electrode. $V_K$ ($K = 1, N$) describe the strength of the chemisorption coupling between the DNA molecule and the reservoirs, and $4\gamma$ is the bandwidth of the reservoir. Through Löwdin’s matrix partition technique [15], the electrode Hamiltonian can be replaced by a self-energy:

$$H_{eff} = \Sigma_1 |1\rangle\langle 1| + \sum_{\alpha=1}^{N} E^0_{\alpha} |\alpha\rangle\langle \alpha| + \sum_{\alpha=1}^{N-1} \beta |\alpha\rangle\langle \alpha+1|$$  

$$+ \Sigma_N |N\rangle\langle N| + h.c.,$$  

(6)

where $\Sigma_K$ ($K = 1, N$) are respectively the self-energy resulting from the coupling of the molecule to the left (right) electrode. The Green’s Function is expressed as

$$G = \frac{1}{(zI - H_{eff})},$$  

(7)

where $z$ is a complex number, whose real part $E$ is the energy of the transfer electrons.

Mujica et al. [10] ignored the electrostatic drop along the molecule. Here we consider the linear voltage drop along the molecule, i.e., the electric potential between the electrodes varying linearly with distance. This assumption is a good approximation to the computed potential profile through the molecule between the two electrodes [17]. Thus the energies of the sites are function of bias $V$:

$$E^0_{\alpha} = E_b - qV_0(\alpha - 1), \quad \alpha = (1, ..., N),$$  

(8)

$$V_0 = V/(N - 1),$$  

(9)
The effective Hamiltonian can be expressed in the following matrix form:

\[
H_{\text{eff}} = \begin{bmatrix}
E_b + \Sigma_1 & \beta & 0 & \cdots & \cdots \\
\beta & E_b - qV_0 & \beta & 0 & \cdots \\
0 & \vdots & \ddots & \ddots & \beta \\
0 & \cdots & 0 & \beta & E_b - (N - 1)qV_0 + \Sigma_N
\end{bmatrix},
\]

where \( q \) is the average effective charge on each site. \( G_{1N} \) can be obtained:

\[
G_{1N} = \frac{(-1)^{N-1} \beta^{N-1}}{|zI - H_{\text{eff}}|},
\]

where \( |zI - H_{\text{eff}}| \) denotes determinant. Then our task is to deduce the expression of \( |zI - H_{\text{eff}}| \). For convenience, we define:

\[
A_n = \begin{bmatrix}
a & \beta & 0 & \cdots & \cdots \\
\beta & a - qV_0 & \beta & 0 & \cdots \\
0 & \vdots & \ddots & \ddots & \beta \\
0 & \cdots & 0 & \beta & a - (n - 1)qV_0
\end{bmatrix},
\]

and from linear algebra knowledge,

\[
G_{1N} = \frac{(-1)^{N-1} \beta^{N-1}}{D_{1N} - D_{1,N-1}\Sigma_N - D_{2,N}\Sigma_1 + D_{2,N-1}\Sigma_1\Sigma_N}
\]

where \( a = E_b - E_F \), i.e. the site’s energy measured from the Fermi energy of the reservoirs without the electric field. \( D_{PQ}(P = 1, 2; Q = N - 1, N) \) is the determinant of the matrix obtained from \( A \) by taking rows and columns only in the range from \( P \) to \( Q \) [10].

We use Generating Function method to obtain \( D_{1N} \). Setting \( A_n = D_{1n} \), and \( A_N = D_{1N} \), we find that \( A_n \) satisfies the following recursion relation:

\[
A_n = [a - (n - 1)qV_0]A_{n-1} - \beta^2 A_{n-2}.
\]

If we define

\[
F(x) = \sum_{n=1}^{\infty} A_n x^n,
\]

then we obtain that

\[
F(x)[1 - ax + \beta^2 x^2] + (qV_0)x^2F'(x) = ax - \beta^2 x^2.
\]
Since \( qV_0 \) is small, we can use a perturbation method, and regard \( qV_0 \) as a perturbation parameter. Up to the first order approximation, we have:

\[
F(x) = F_0(x) + (qV_0)F_1(x),
\]

\[
F_0(x) = -1 + \frac{1}{1-ax + \beta^2 x^2},
\]

\[
F_1(x) = \frac{-x^2 F_0'(x)}{(1-ax + \beta^2 x^2)},
\]

Then we decompose \( F(x) \) into a sum of several fractions, and expand them to a power series, and obtain the \( A_n \):

\[
A_n = A_n^{(0)} + (qV_0)A_n^{(1)},
\]

\[
A_n^{(0)} = \frac{1}{2^{n+1}} \left( a + \sqrt{a^2 - 4\beta^2} \right)^{n+1} - \left( a - \sqrt{a^2 - 4\beta^2} \right)^{n+1},
\]

\[
A_n^{(1)} = -\frac{\beta^{2n-1}}{8\mu^3} (n-1)(\lambda_1^n - \lambda_2^n)[1 + n(1 - \alpha^2 + \alpha \mu \frac{\lambda_1^n + \lambda_2^n}{\lambda_1^n - \lambda_2^n})],
\]

\[
\alpha = \frac{a}{2\beta},
\]

\[
\mu = \sqrt{\alpha^2 - 1},
\]

\[
\lambda_1 = \frac{\alpha - \sqrt{\alpha^2 - 1}}{\beta},
\]

\[
\lambda_2 = \frac{\alpha + \sqrt{\alpha^2 - 1}}{\beta}.
\]

In terms of our convention, \( A_N \) is the determinant \( D_{1,N} \). Using similar steps, we can obtain \( D_{1,N-1}, D_{2,N}, D_{2,N-1} \), and then obtain \( G_{1,N} \). It is straightforward to perform similar calculations for high order perturbation.

Then, we can calculate the current through the single molecular dsDNA using wide energy band approximation. We assume \( \Delta_K (K = 1, N) \) to be energy independent. For convenience, we consider that the two electrodes have identical Fermi energies, which are set to zero. For DNA molecules in equilibrium, the bases of DNA are neutral, while in transport process, there are charges introduced by the contacts, and charges in DNA will be redistributed. Since the average charge \( q \) on each site is small, the derivation of the actual potential drop along DNA molecule from the assumed linear drop can be ignored.

In previous efforts, many papers ignored the situation that the sites’ energies will vary along the molecular wire because of the voltage drop in high-intensity electric field. Some papers did consider this effect (e.g., Ref. [16]), but they did not obtain an analytic expression of the differential conductance. The present paper achieves this task. In general, the
modified Hamiltonian is more complex. Since the Green’s Function must be obtained by calculating the inverse matrix, it is not a trivial task, especially when the matrix is large.

Using the linear voltage drop approximation, we first obtain the explicit expression of $G_{1N}$ up to the first order perturbation, and get a more reasonable current-voltage relation. We show the I-V curve in Fig.1 for a 4-nucleotide DNA, and Fig. 2 for a 30-nucleotide DNA. We find when considering the voltage drop in the molecule, the current-voltage curves always become much steeper near the threshold. This is in accordance with the experiment of Porath et al. [9]: some I-V curves in their paper are much steeper near the threshold. Our result is intuitional, because voltage drop effect makes the electron transport more easily in strong electric field. Moreover, Fig. 3a of Porath’s paper contains two different I-V characteristics of the same 30-base pair DNA sample. The difference between these two curves may be the result of a sudden change in the DNA wire, possibly a conformational change. In transport process, the charge distribution along DNA may depend on DNA’s chemical nature, for example, the molecule’s conformation. Although there was a similar voltage drop in the sample of both cases, the observed electrostatic drop effect are different. Finally, our work can be used to calculate other molecular wires. Since the computational complexity of our analytical deduction is not sensitive to the number of sites, so we can calculate long chains.

An issue of interest is to investigate theoretically the transport property of DNA molecules made of heterogeneous base sequences. We are now working on this possibility.

In summary, we consider the electrostatic potential across the DNA, which may change the site energy along the DNA with the applied bias. This made the computation more difficult. We have proposed an analytical computational method to deal with this difficulty. It can be used to calculate the I-V characteristic of homogeneous DNA wires of arbitrary length. We can use the potential drop effect to explain recent single molecular DNA experiments.

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* Email address: muwh@itp.ac.cn
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FIG. 1: Theoretically predicted current-voltage characteristics of single molecular double stranded DNA. Parameters: $\beta = -2.4eV$, $V_1 = V_N = 0.5eV$, $\gamma = 10.0eV$, $N = 4$, and $E_b$ is 1.0eV below $E_F$. The full line is calculated with $q = 0$, i.e., no site’s energy shift effect. The dashed curve is calculated with $q = 0.05e$. The dotted curve is calculated with $q = 0.1e$. 

FIG. 2: Theoretically predicted current-voltage characteristic of single molecular double stranded DNA. Parameters: $\beta = -0.1eV$, $V_1 = V_N = 3.0eV$, $\gamma = 10.0eV$, $N = 30$, and $E_b$ is 1.0eV below $E_F$. The full line is calculated with $q = 0$, i.e., no site’s energy shift effect. The dashed curve is calculated with $q = 0.01e$. The dotted curve is calculated with $q = 0.05e$. 