

Electronic Conduction in Short DNA Wires

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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 makes the current-voltage curve steeper beyond certain threshold than without considering it, which accords well with recent experiments. The present method can also be used to calculate the current-voltage characteristics for other molecular wires of arbitrary length.

Recently, the progress of molecular wires [1] attracts much attention on the transport behavior of molecular wires. A number of experimental groups have reported measurements of the current-voltage (I-V) characteristics of molecules, especially Deoxyribonucleic Acid (DNA)[2, 3]. DNA has a special double-helix structure with complementary nucleotide base-pairs stacking onto each other, which could possibly make DNA a good candidate as a media for one-dimensional electronic transport[4]. Intense experimental investigations have already been made on the transport property of DNA[5]. Using scanning tunneling microscope technique, Dunlap *et al.* [6] found that DNA is an insulator. Fink and schoenenberger [7] 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.* [8] measured small number of molecules, and observed proximity-induced superconductivity. In particular, Porath *et al.* [9] directly measured electrical transport through individual DNA molecules, and suggested DNA to be a semiconductor with a voltage gap. To explain experimental facts, several theoretical models which range from the Hückel model [10] to the density functional theory [11, 12] have been developed.

In the present paper, we investigate theoretically Porath's experiment [9] 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 *et al.* [10]. The model Hamiltonian can be written as the sum of two terms,

$$H = H^0 + H', \quad (1)$$

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 [10]

$$H^0 = \sum_i E_i^0 |i\rangle\langle i| + \sum_{\alpha=1}^N E_{\alpha}^0 |\alpha\rangle\langle\alpha| + \sum_f E_f^0 |f\rangle\langle f| + \quad (2)$$

$$\sum_{\alpha=1}^{N-1} \beta |\alpha\rangle\langle\alpha+1| + h.c.$$

$$H' = \sum_i V_{i1} |i\rangle\langle 1| + \sum_f V_{Nf} |N\rangle\langle f| + h.c., \quad (3)$$

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_{i1} (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]:

$$g = \frac{2e^2}{\pi\hbar} |G_{1N}|^2 \Delta_A(E_f)\Delta_B(E_f), \quad (4)$$

where G_{1N} is the $(1N)$ element of the matrix formula Green's Function G , it is related to the molecule's site 1 and N . Δ_1 and Δ_N are semielliptical reservoir spectral densities defined through Newns' chemisorption theory [14]:

$$\Delta_K(E) = \begin{cases} \frac{V_K^2}{\gamma} \sqrt{1 - (E/2\gamma)^2}, & |E/2\gamma| < 1, \\ 0, & |E/2\gamma| > 1, \end{cases} \quad (5)$$

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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 4γ is the bandwidth of the reservoir. Through Löwdin's matrix partition technology [15], the electrode Hamiltonian can be replaced by a self-energy:

$$H_{eff} = \Sigma_1 |1\rangle\langle 1| + \sum_{\alpha=1}^N E_{\alpha}^0 |\alpha\rangle\langle\alpha| + \sum_{\alpha=1}^{N-1} \beta |\alpha\rangle\langle\alpha+1| + \Sigma_N |N\rangle\langle N| + h.c., \quad (6)$$

where Σ_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

$$G = \frac{1}{(zI - H_{eff})}, \quad (7)$$

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 [18]. Thus the energies of the sites are function of bias V :

$$E_{\alpha}^0 = E_b - qV_0(\alpha - 1), \quad \alpha = (1, \dots, N), \quad (8)$$

$$V_0 = V/(N - 1), \quad (9)$$

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

$$H_{eff} = \begin{bmatrix} E_b + \Sigma_1 & \beta & 0 & \dots & \dots \\ \beta & E_b - qV_0 & \beta & 0 & \dots \\ 0 & \vdots & \ddots & \ddots & \beta \\ 0 & \dots & 0 & \beta & E_b - (N - 1)qV_0 + \Sigma_N \end{bmatrix}, \quad (10)$$

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

$$G_{1N} = \frac{(-1)^{N-1} \beta^{N-1}}{|zI - H_{eff}|}, \quad (11)$$

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

$$A_n = \begin{bmatrix} a & \beta & 0 & \dots & \dots \\ \beta & a - qV_0 & \beta & 0 & \dots \\ 0 & \vdots & \ddots & \ddots & \beta \\ 0 & \dots & 0 & \beta & a - (n - 1)qV_0 \end{bmatrix}, \quad (12)$$

and from linear algebra knowledge,

$$G_{1N} = \frac{(-1)^{N-1} \beta^{N-1}}{D_{1,N} - D_{1,N-1} \Sigma_N - D_{2,N} \Sigma_1 + D_{2,N-1} \Sigma_1 \Sigma_N} \quad (13)$$

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:

$$A_n = [a - (n - 1)qV_0]A_{n-1} - \beta^2 A_{n-2}. \quad (14)$$

If we define

$$F(x) = \sum_{n=1}^{\infty} A_n x^n, \quad (15)$$

then we obtain that

$$F(x)[1 - ax + \beta^2 x^2] + (qV_0)x^2 F'(x) = ax - \beta^2 x^2. \quad (16)$$

Since qV_0 is small, we could use a perturbation method, and regard qV_0 as a perturbation parameter. Up to the first order approximation, we have:

$$F(x) = F_0(x) + (qV_0)F_1(x), \quad (17)$$

$$F_0(x) = -1 + \frac{1}{1 - ax + \beta^2 x^2}, \quad (18)$$

$$F_1(x) = \frac{-x^2 F_0'(x)}{(1 - ax + \beta^2 x^2)}. \quad (19)$$

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

$$\begin{aligned} A_n &= A_n^{(0)} + (qV_0)A_n^{(1)}, \\ A_n^{(0)} &= \frac{1}{2^{n+1}} \frac{(a + \sqrt{a^2 - 4\beta^2})^{n+1} - (a - \sqrt{a^2 - 4\beta^2})^{n+1}}{\sqrt{a^2 - 4\beta^2}}, \\ A_n^{(1)} &= -\frac{\beta^{2n-1}}{8\mu^3} (n-1)(\lambda_1^n - \lambda_2^n) [1 + n(1 - \alpha^2 + \alpha\mu \frac{\lambda_1^n + \lambda_2^n}{\lambda_1^n - \lambda_2^n})], \\ \alpha &= \frac{a}{2\beta}, \\ \mu &= \sqrt{\alpha^2 - 1}, \\ \lambda_1 &= \frac{\alpha - \sqrt{\alpha^2 - 1}}{\beta}, \\ \lambda_2 &= \frac{\alpha + \sqrt{\alpha^2 - 1}}{\beta}. \end{aligned} \quad (20)$$

In terms of our convention, A_N is nothing but 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 $G_{1,N}$. Obviously, 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 the zero point of the energy. 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 variate along the molecular wire because of the voltage drop in high-intensity electric field. Some papers did consider this effect (e.g., Ref. [17]), but they failed to obtain an analytic expression of the differential conductance. The present paper achieves this hard 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 $G_{1,N}$ 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

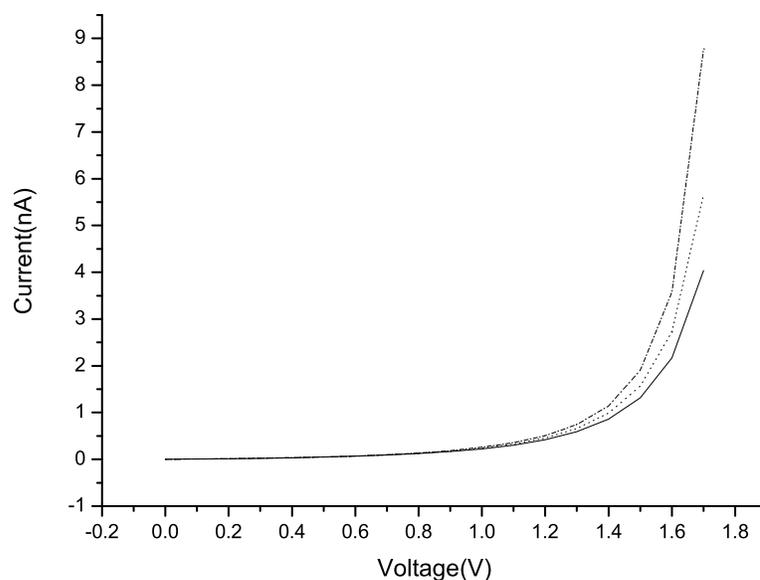


FIG. 1: Theoretically predicted current-voltage characteristics of single molecular double stranded DNA. Parameters: $\beta = -2.4eV$, $V_1 = V_N = 0.5eV$, $\gamma = 10.0eV$, $N = 4$, and E_b is $1.0eV$ below E_F . The full line is calculated with $q = 0$, i.e., no site's energy shift effect. The dashed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

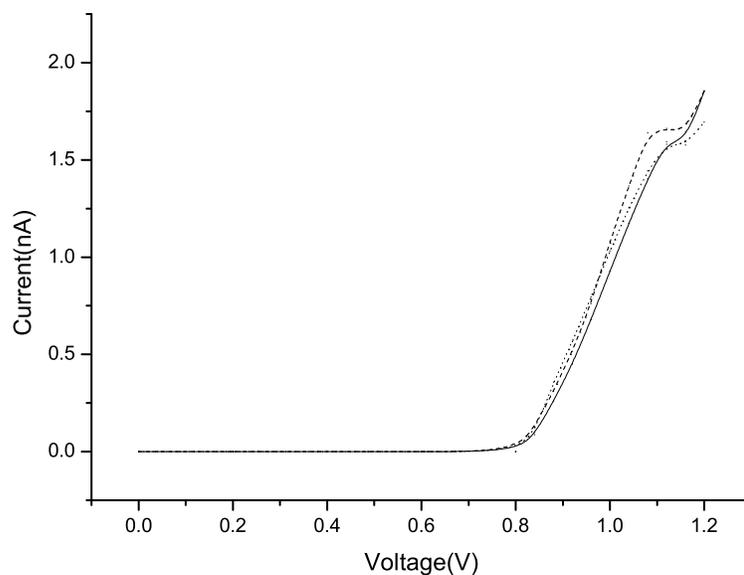


FIG. 2: Theoretically predicted current-voltage characteristic of single molecular double stranded DNA. Parameters: $\beta = -0.1eV$, $V_1 = V_N = 3.0eV$, $\gamma = 10.0eV$, $N = 30$, and E_b is $1.0eV$ below E_F . The full line is calculated with $q = 0$, i.e., no site's energy shift effect. The dashed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

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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